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AMERICAN LEATHER CHEMISTS ASSOCIATION

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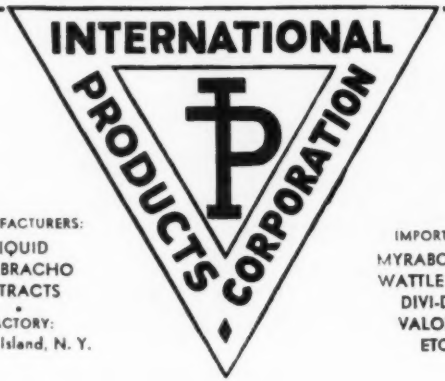

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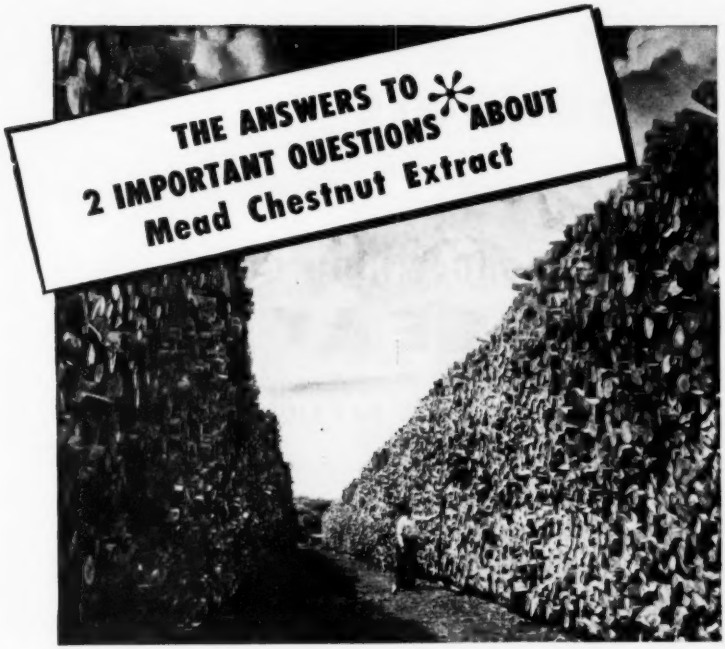

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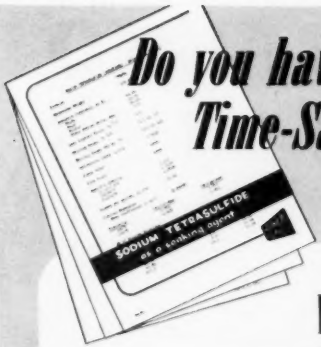

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4937.

Fig. 2, showing appearance of "magic eye" before and after reaching endpoint.

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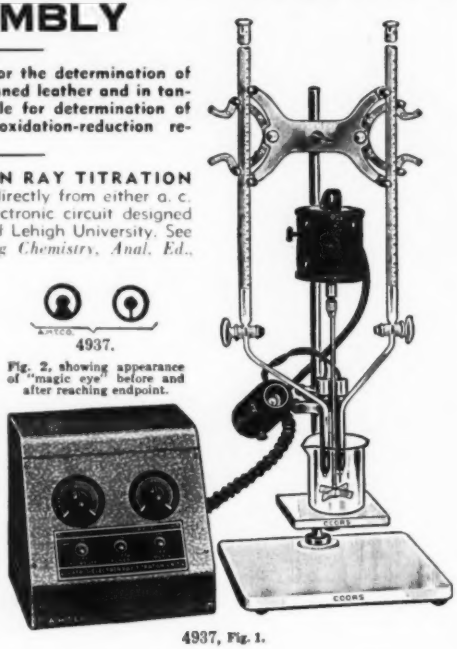

4937, Fig. 1.

4937. Electron Ray Titration Assembly, Serfass, complete assembly as shown in illustration, consisting of control unit with electron ray tube, titration stand complete with base and swinging shelf of Coors porcelain, paired burettes, clamps, platinum and tungsten electrodes with holder, and stirring apparatus with speed control rheostat and motor for 115 volts, 60 cycles, single phase a.c. With detailed directions for use including step by step procedures for typical titrations and preparation of standard solutions **159.92**

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REPORT OF THE MINERAL LEATHER COMMITTEE

In 1950, at the convention in French Lick, the Mineral Leather Committee, under the chairmanship of the writer, initiated a program revising and improving the "Methods of Sampling and Analysis" under the heading "D-Chrome Tanned Leather" which were adopted as Provisional in 1946.

The committee work centered around the determination of the total sulfates because, in the light of more recent investigations, the old Provisional Method which is based on a paper by Thomas [1] does not allow the barium sulfate to be precipitated under optimal conditions. Among the various reagents which could be used to replace the alkali phosphates heretofore employed, ammonium hydroxide seemed to be the most logical choice. It had been successfully used by several authors [2] although under varying experimental conditions, and it allowed aliquots of the solutions to be used for the estimation of organic acids [3].

TABLE I

Neutral Sulfate in Air Dry Leather for Different Immersion Times

	45 min.	90 min.	120 min.
Gm. $BaSO_4$ for neutral sulfates	0.0113	0.0123	0.0136
Ml. 0.01 N alkali	8.5	8.9	8.64
Number of participants	7	7	3
Number of Digestions	19	19	5

The directions sent out to members of the Committee in 1950 contained a number of additional small changes to which no oppposition arose. They are incorporated in the version printed following this report.

The members of the committee who received the first sample of undyed one bath chrome leather were asked to submit not only figures for total sulfate, but also figures for neutral sulfate and for the titration of the aqueous digestion which is to be converted to per cent SO_3 in accordance with the directions given in the "Methods." Most of these figures were received after an immersion time of 45 and 90 minutes and only a few after 2 hours, which is the immersion time of the old Provisional Method, and which upon request of several committee members has not been shortened in the new version printed below.

The figures received for total sulfate are omitted from the above table I summarizing the results of the initial work, because after they were received it was felt that more work on the determination of total sulfates was neces-

1. Thomas, JALCA **15**, 504 (1920)
2. Theis & Meerbott, JALCA **37**, 293 (1942) — Seligsberger, JALCA **43**, 227 (1948).
3. Seligsberger JALCA **43**, 227 (1948) — Proposed Methods for Anal. of Chrome-Vegetable Retan Leathers, JALCA **44**, 633 (1949).

TABLE II

Ammonia vs. Phosphate Method for Total Sulfate

ANALYST	AMMONIA METHOD (A)					PHOSPHATE METHOD (B)					Diff. Between Method (B-A)
	Series I	Series II	Average	Diff. between dups.	Diff. from gen. avg.	Series I	Series II	Average	Diff. between dups.	Diff. from gen. avg.	
	g. $BaSO_4$ in aliquot of 1 g. air dry leather					g. $BaSO_4$ in aliquot of 1 g. air dry leather					
Benrud	.0840	.0843	.0842	.003	+.0016	.0837	.0857	.0847	.0020	−.0002	+.005
Ewe-Weaver	.0835	.0824	.0830	.0011	+.0004	.0766	.0795	.0781	.0029	−.0068	−.0049
Henrich	.0819	.0827	.0823	.0008	−.0003	.0838	.0838	.0838	.0000	−.0011	+.0015
Adams	.0833	.0828	.0831	.0005	+.0005	.0886	.0855	.0871	.0031	+.0022	+.0040
Seligsberger	.0780	.0795	.0788	.0015	−.0038	.0840	.0830	.0835	.0010	−.0014	+.0047
Turley-Wendkos	.0842	.0841	.0842	.0001	+.0016	.0918	.0920	.0919	.0002	+.0070	+.0077
General Average		-	.0826					.0849			+.0023
Median			.0831					.0843			
Variance*			401					2066			
Standard Deviation*			20					45			
Probable error*			13					30			

*In tenths of mg.

For variance of the 2 methods:

$$F = \frac{2066}{401} = 5.15$$

$n1 = n2 = 6$

Significant at 0.05 level

For difference between the 2 methods:

$T = 0.366$ (10 degrees of freedom)

not significant at 0.10 level

sary. Table I represents the only data ever reported by a committee on the water diffusion method for neutral sulfate. In order to save space, only the averages of the figures received by the various co-workers are shown. As far as the individual results are concerned, this much may be said. The agreement between laboratories was not a very high one, but the figures obtained by any one individual were very consistent. A conversion of the titration figures into per cent SO_3 shows that the leather in question contained practically no neutral sulfate.

At the 1951 convention in Groton, it was decided to make a full comparison between the ammonia and the phosphate method. The figures obtained by the 6 participants are reproduced in table II. Although the material was somewhat scanty for a statistical treatment, Merrill undertook a statistical analysis which he interpreted as follows:

(1) Agreement between duplicates is better by the ammonia method.

(2) Agreement between laboratories is better by the ammonia method.

(3) The slightly higher average yielded by the phosphate method is not significant, in view of the relatively small average difference of only 2.3 mg., and because of the relatively large variations in the individual differences.

After completion of this work, all committee members were willing to go along with a recommendation to Council of the ammonia method. However in view of the rather significant discrepancies still existing between the individual workers, Council felt some additional work of the ammonia method would be distinctly worthwhile. In this work the ammonia was used at higher and lower concentrations than before, so as to establish the fact that the concentration prevailing in the new method is not in any way critical. The data obtained by 7 committee members in this study of the ammonia method are reproduced in table III. At a glance it can be seen that the agreement between laboratories is much better than in the preceding work.

In treating Table III statistically, H. B. Merrill found by application of the t test that 0.1N ammonia gave results significantly higher than those obtained with 0.05N ammonia. The difference between 0.15N and 0.1N ammonia was not significant. Consequently the Proposed Method for Determining Acid Sulfate in Chrome-Vegtable Retan Leather [3] ought to specify the use of 0.1N ammonia.

While the differences between laboratories may not be important, they are significant. Agreement between duplicates in any one laboratory is much better than agreement between different laboratories. The cause of these inter-laboratory differences has not been investigated.

The findings of table III have been submitted to Council at its recent session. The Council moved to submit the new version of the methods in

TABLE III

Total Sulfates Obtained by Various Concentrations of Ammonium Hydroxide.

Worker & Tools Used	Molarity of Ammonium Hydroxide	g. $BaSO_4$ in aliquot of 1 g. airdry leather Series I	Series II	Avg.	Diff. between Dups.	Diff. from Gen. Avg.
Benrud	0.15	.0902	.0880	.0891	.0022	.0007
(Porc. cruc.	0.10	.0880	.0884	.0882	.0004	.0019
Muffle)	0.15	.0876	.0868	.0872	.0008	.0022
Ewe/Weaver	0.15	.0890	.0887	.0889	.0003	.0009
(Gooch cruc.	0.10	.0913	.0918	.0916	.0005	.0015
Muffle)	0.05	.0904	.0884	.0894	.0020	.0000
Henrich	0.15	.0897	.0890	.0894	.0007	.0004
(Porc. cruc.	0.10	.0890	.0892	.0891	.0002	.0010
Burner)	0.05	.0888	.0882	.0885	.0006	.0009
Merrill/Adams	0.15	.0911	.0908	.0910	.0003	.0012
(Gooch cruc.	0.10	.0907	.0912	.0910	.0005	.0009
Burner)	0.05	.0904	.0911	.0908	.0007	.0014
Seligsberger	0.15	.0905	.0900	.0903	.0005	.0005
(Porc. cruc.	0.10	.0910	.0905	.0908	.0005	.0007
Burner)	0.05	.0905	.0900	.0903	.0005	.0009
Theis	0.15	.0898	lost	———	———	———
—	0.10	.0901	.0898	.0890	.0003	.0011
	0.05	.0894	.0907	.0901	.0013	.0007
Turley/Wendkos	0.15	.0903	.0910	.0907	.0007	.0009
(Gooch cruc.	0.10	.0912	.0896	.0904	.0016	.0003
Muffle)	0.05	.0896	.0894	.0895	.0002	.0001
General Average	0.15	.0898	Diff:	+0.0003		
	0.10	.0901		—0.0007		
	0.05	.0894				

t (calc. by Youden's method[4])

for a comparison of 0.15 and 0.10 molar solutions = 0.785 (not significant)

for a comparison of 0.10 and 0.05 molar solutions = 2.812 (significant since critical value is 2.16 on the 5% level.)

4. Youden's Statistical Method for Chemists, pp. 27–29.

Section D of the ALCA method to its membership for approval as Provisional.

In accordance with a motion passed in Groton last June, the acidity (pH) method of the Federal Specifications KKL-311 has also been included in this new version.

L. SELIGSBERGER, *Chairman.*

Received April 24, 1952.

PROPOSED NEW VERSION OF PROVISIONAL METHOD
D — Chrome Tanned Leathers

SULFATES

Total Sulfates:

To 1 g. of ground leather in a 250 ml. volumetric flask [1] add 200 ml. of a 0.1N ammonium hydroxide solution [2]. Immerse the flask up to the neck in a bath of boiling water for two hours and see that all particles are thoroughly wetted by swirling occasionally. Cool rapidly to room temperature, make up to volume with distilled water, shake well and without delay filter through a folded filter paper, discarding the first 20 to 25 ml. of the filtrate. Pipette 200 ml. of the filtrate into a 600 ml. beaker, add about 20 ml. 1.5 N hydrochloric acid [3]. Heat to boiling, and while boiling and stirring the solution add dropwise 20 ml. of a one per cent solution of barium chloride. Keep the covered beaker in a warm place without further boiling, at least for two hours and preferably overnight.

Filter through a fine-grained ashless filter paper (e. g. Whatman #42) and wash the precipitate on the paper eight times with hot water, or until free from chlorides. Transfer the paper and precipitate to a weighed porcelain crucible and ignite gently, either over a gas burner or in a muffle oven at 900°C for one hour. If desired, a Gooch or porous porcelain filter crucible may be used to collect the precipitate.

SO_3 per cent : gms. $BaSO_4$ x 42.875

Water Soluble Sulfates:

Proceed as described under total sulfates, but use distilled water. Cool, make up to volume and filter as before. Transfer 200 ml. to a beaker.

(b) Free (or water soluble) acid: Titrate with 0.01 N sodium hydroxide, using methyl red methylene blue indicator [4].

SO_3 per cent : ml. 0.01 N NaOH x 0.05

(a) Add 4 to 5 ml. 1.5 N hydrochloric acid (see above), heat to boiling and while boiling add 10 ml. of a one per cent barium chloride solution, drop by drop. Proceed as for total sulfates and weigh as $BaSO_4$.

SO_3 per cent : gms. $BaSO_4$ x 42.875

Neutral Sulfates: SO_3 per cent = a - b

Combined Sulfates: SO_3 per cent : Total SO_3 - Neutral SO_3.

Basicity

Express basicity according to Schorlemmers' system[5], employing the following equation:

$$\text{sulfate acidity} = \frac{\text{per cent combined } SO_3}{\text{per cent } Cr_2O_3} \times 63.3$$

per cent basicity = 100 - per cent acidity
(only when no other anions are present)

When other metals that form hydrolyzable sulfates are present, their presence in the leather may be taken into consideration when basicity is computed. The following conversion factors may be used:

Al_2O_3	to	Cr_2O_3	: 1.49
ZrO_2	to	Cr_2O_3	: 0.82
Fe_2O_3	to	Cr_2O_3	: 0.95

Chlorides

Chlorides are completely removed from leather by the ammonia extraction method. They may be determined in an aliquot of the filtrate, if so desired. This aliquot is first neutralized by careful addition of a dilute acetic acid solution, using methyl orange indicator, and is titrated with 0.1 N silver nitrate in presence of a few drops of potassium chromate.

1. A. H. Thomas catalog, 1950 ed., No. 5528, page 648, for a convenient wide-neck Pyrex flask of this size.
2. 14 ml. reagent grade conc. ammonium hydroxide (NH_2 28 per cent minimum by weight) to 2000 ml.
3. 125 ml. reagent grade conc. hydrochloric acid (HCl 37 per cent minimum) to 1000 ml.
4. a mixture of equal volumes of 0.2 per cent methyl red in alcohol and 0.1 per cent methylene blue in alcohol.
5. See c-1 Chrome Tanning Materials—Basicity.

Received May 5, 1952

A New Iron Tannage*

By W. O. Dawson

Chemtan Company

The purpose of this investigation was to replace both chromium salts and vegetable tannins in the manufacture of stuffed army retan upper leather. Until recently the many attempts to produce commercial iron leather were not successful because the inorganic iron salts used hydrolyzed very readily and thus reduced the aging resistance of the leather. Also, these salts by them-

*Presented at the Forty-Seventh Annual Meeting of the A. L. C. A., Groton, Conn., June 12, 1951.

selves will not permit neutralization to the required pH for iron tannage without precipitating. After the maximum degree of tannage was obtained, further neutralization would cause detanning of the leather by removal of the iron salt. The leather tanned with these salts was inferior to chrome tanned leather in regard to fullness, pliability and strength.

More recently, the effect of complex forming salts has been investigated, and it appears from the literature that sulfophthalic acid (Ferrigan P) and gluconic acid [1, 2] are the most promising. In this investigation these and other hydroxy carboxylic acids as complex formers were examined. The earlier findings were confirmed. The hydroxy carboxylic acid complex salt can be neutralized to the desired pH range for tanning without precipitating, the leather has a much higher Ts, and is comparatively full and soft. On the other hand, our investigation shows conclusively that stabilization of the tannage over a pH range sufficiently wide for practical application is not attained: when increasing the neutralization beyond the pH of optimum Ts, drastic detanning occurs. Also, this leather is still inferior to chrome leather in regard to fullness and strength.

We have found that through the use of certain amino-aldehyde resins in conjunction with a gluconic acid ferric sulfate complex salt, the remaining obstacles to a practical iron tannage are eliminated. The leather is much more resistant to detanning, has good strength and compares favorably with chrome leather in regard to fullness. This process has been applied on a production basis by a well known tanning firm on stuffed army retan upper side leather, and fatliquoring elk side leather. These leathers were indistinguishable from regular chrome tanned, vegetable retanned leathers, have met all applicable Government specifications, and the Quartermaster General's Office is now conducting extensive aging and wear tests. Accelerated aging tests were started during August of 1950, and as of this date the leather has been found to be perfectly satisfactory.

Experimental

All percentages were based on the drained pickled weight of the skin. Pieces of pickled goatskin were cut into squares, immersed in 200 per cent liquor containing 10 per cent NaCl and 15 per cent of $Fe_2(SO_4)_3 \cdot 9\ H_2O$ plus the specified amount of the sodium salt of the organic acid. The pieces were drummed over night and neutralized the next morning by adding increasing amounts of a sodium carbonate solution in additions one hour apart, taking pH and Ts measurements before each addition of alkali. It was assumed that the tanning liquor was adjusted to equilibrium in the allowed neutralization time because several samples were drummed over night, and the pH of the solution dropped no more than 0.1 of a unit.

FIGURE I

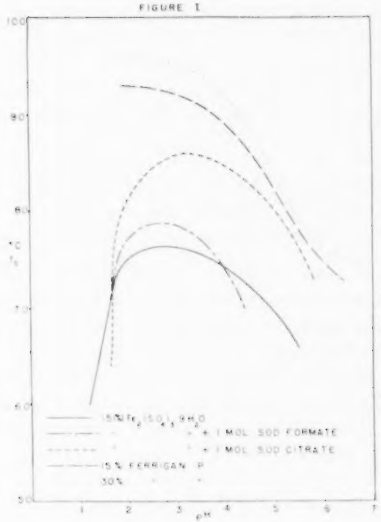
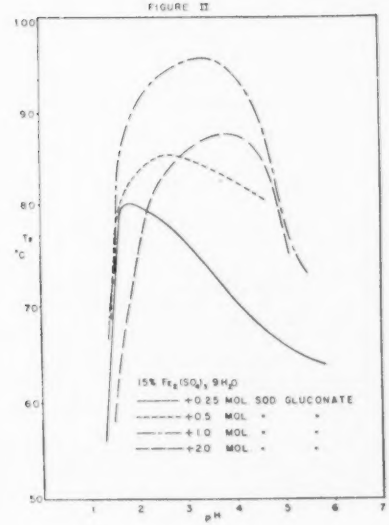


FIGURE II



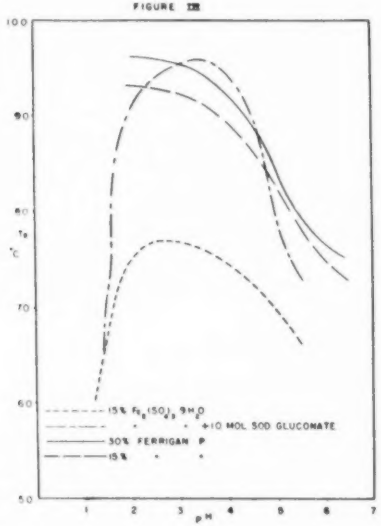
In Figure I it can be seen that ferric sulfate alone raised the Ts of the skin to a maximum of 75°C. The addition of 1 mol of sodium formate to the ferric sulfate increased the maximum Ts only to 78°C. The use of 15 per cent of Ferrigan P produced a maximum Ts of 93°C. and 30 per cent Ferrigan P a Ts of 96°C. The addition of 1 mol of sodium citrate increased the maximum Ts to 86°C.

In Figure II the use of 0.25 mol of sodium gluconate per mol of ferric sulfate produced a maximum Ts of 81°C, 0.5 mol of sodium gluconate a maximum Ts of 86°C, 1 mol 96°C, and 2 mols 88°C.

The examination of Figures I and II indicate that:

Formic acid has little influence on Ts, citric acid more, and gluconic acid the most pronounced effect in this series, as can be anticipated from the increasing number of hydroxyl groups in the molecule. Also it is shown that there is an optimum amount of gluconic acid beyond which the Ts decreases again. The high Ts of the Ferrigan P leathers in this application indicates that the number of hydroxyl groups is not the only criterion for the effect of the organic salt on Ts.

FIGURE III



In Figure III the curves from Figures I and II demonstrating the influence of neutralization on Ts of ferric sulfate alone and with 1 mol of sodium gluconate, and of 15 per cent and 30 per cent of Ferrigan P are presented.

Maximum Ts is obtained with ferric sulfate alone at pH 2.5 with a Ts of 76°C, with the addition of 1 mol of sodium gluconate at pH 3.5 with a Ts of 96°C, with 15 per cent of Ferrigan P at pH 2.0 with a Ts of 93°C, and with 30 per cent of Ferrigan P at pH 2.1 with a Ts of 96°C. When the pH is raised above these maximum points, the Ts decreases drastically, and at pH 5.0 the Ts of the leather tanned with ferric sulfate alone has dropped from a maximum of 76°C, to 67°C, with the addition of 1 mol of sodium gluconate from 96°C, to 82°C, with 15 per cent Ferrigan P from 93°C, to 81°C, and with 30 per cent Ferrigan P from 96°C, to 84°C.

The practical significance of these findings is that penetration of these tanning materials through heavy stock requires a strongly acid solution. The maximum Ts is then obtained through neutralization, but since the pH at this point is still quite low, any subsequent operation which raises the pH will tend to detan the leather. The results clearly show that the most promising iron salts thus made do not produce a sufficiently stable tannage. Regardless of what the exact chemical combination between collagen and the iron salts may be, it is evident that the bonding effect is not sufficiently strong or permanent for the conditions applying in practical tanning. The organic ferric complex salts are negatively charged, and it has occurred to us to improve the bonding effect by establishing a strong positive charge in the collagen, and thus to create a more stable tannage. We have succeeded in accomplishing this by treating the collagen with an amino-aldehyde resin having reactive groups capable of combining with collagen, and being strongly cationic in electrical charge. The resin should not only be water soluble and infinitely dilutable but at least partially polymerized prior to application so as to avoid, during the tanning operation, the uncertainties attending a polymerization process involving very difficult control of pH, salt concentration, temperature, dilution and possibly other factors.

Such a resin is now being produced on a commercial scale and will be called Amino-Aldehyde Resin No. 1.*

Experimental

The best method for applying the Amino-Aldehyde Resin No. 1 is to depickle the stock to pH 7.0–8.0, wash to remove the neutral salts, and drain. The specified amount of Resin is then applied in approximately 60 per cent water and drummed until penetration of the Resin is obtained, which depends upon the thickness of the stock being treated. In the case of goatskins or calfskins this is accomplished in approximately 2 hours, and in unsplit side leather in 4–5 hours. Five per cent of NaCl is then added and drummed for 5 minutes, followed by the addition of the pickle acid and drumming for 30 minutes. The iron salt is added and the process finished as described before.

*Chemtan R-33

FIGURE IX

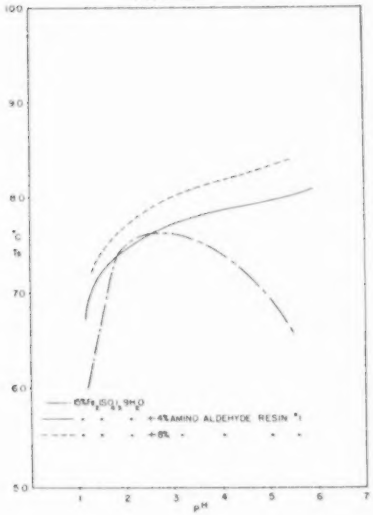
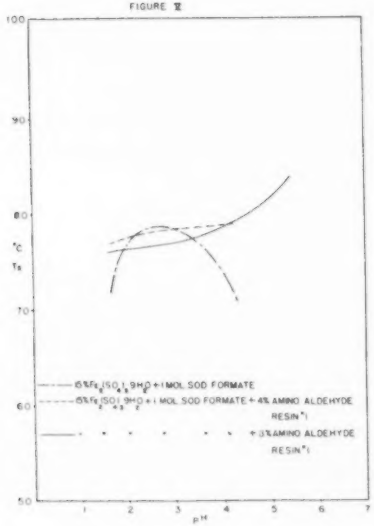


FIGURE X



The Ts of the leather treated with 4 per cent of the Amino-Aldehyde Resin No. 1 prior to acidification was 81°C, and when treated with 8 per cent of the Resin, it was 85°C.

Figure IV demonstrates that the use of 4 per cent of the Resin in conjunction with ferric sulfate influences the Ts to the point that as neutralization is increased to pH 5.5, the Ts also increases. This is also true when 8 per cent of the Resin is used.

Figure V shows that the same result occurs when the Resin is used with the formate-ferric sulfate complex as when it is used with the straight ferric sulfate.

FIGURE XII

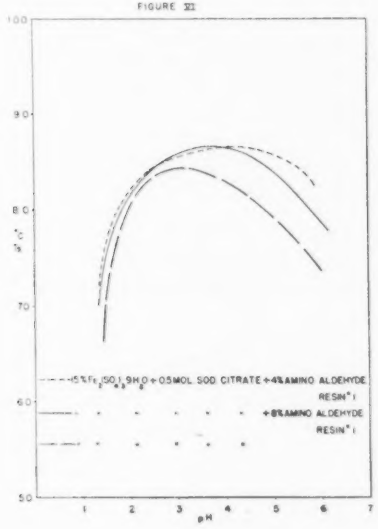


Figure VI demonstrates that when either 4 per cent or 8 per cent of the Resin is used in conjunction with 0.5 mol sodium citrate per mol ferric sulfate complex, the maximum Ts is raised and the Ts is also much higher at pH 5.5.

Figure VII demonstrates that when either 4 per cent or 8 per cent of the Resin is used in conjunction with 1 mol of sodium citrate per mol ferric sulfate complex, the maximum Ts is raised and the Ts is also much higher at pH 5.5.

FIGURE XII

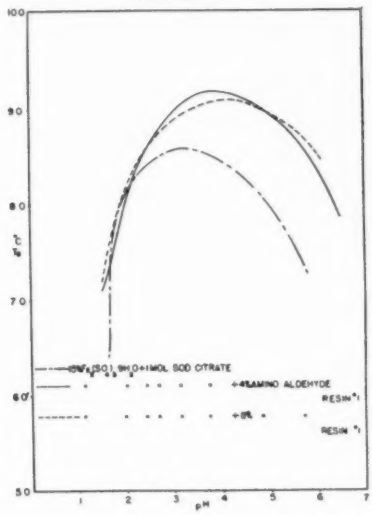
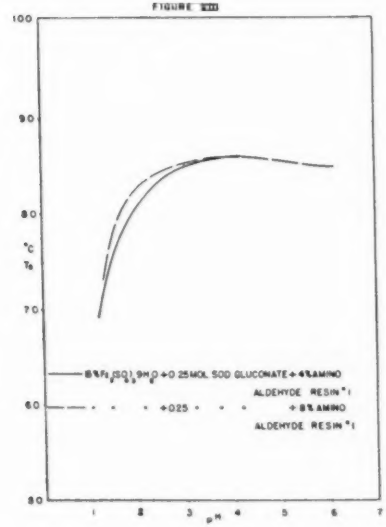
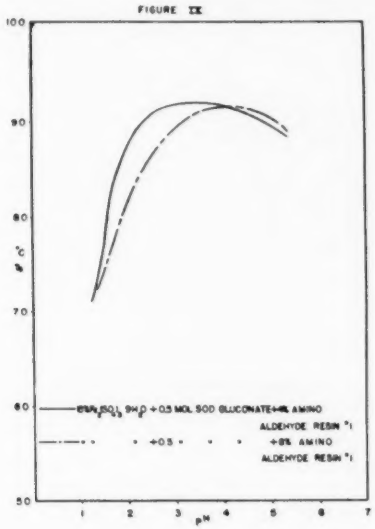


FIGURE XIII





Figures VIII and IX demonstrate that when either 4 per cent or 8 per cent of the Resin is used in conjunction with these gluconate ferric sulfate complex salts, (0.25:1 and 0.5:1 mol ratio) the maximum Ts is raised and the Ts at pH 5.5 is also higher.

Figure X demonstrates that the use of 4 per cent of the Resin with the gluconic acid ferric sulfate complex salt (1:1 mol ratio) results in raising the maximum Ts from 96°C, to 97°C., and at pH 5.5 the Ts is raised from 73°C. to 93°C. The use of 8 per cent Resin improves the results obtained with 4 per cent only very slightly.

Figure XI shows that the use of 4 per cent Resin with the gluconic acid ferric sulfate complex salt (2:1 mol ratio) results in raising the maximum Ts from 88.5°C. to 92.5°C., and at pH 5.5 the Ts is raised from 75°C. to 82°C. The use of 8 per cent Resin raises the maximum Ts from 88.5°C. to 95°C. and at pH 5.5 the Ts is raised from 75°C. to 90.5°C.

Figure XII shows that the use of 4 per cent Resin with 15 per cent Ferrigan P raises the maximum Ts from 93°C. to 95°C., and at pH 5.5 the Ts is also raised from 77°C. to 82°C. The use of 8 per cent Resin raises the maximum Ts to 94°C., and at pH 5.5 to 87.5°C.

Figure XIII demonstrates that the use of 4 Per cent Resin with 30 per cent Ferrigan P raises the maximum Ts from 96°C. to 97°C., and at pH 5.5

FIGURE X

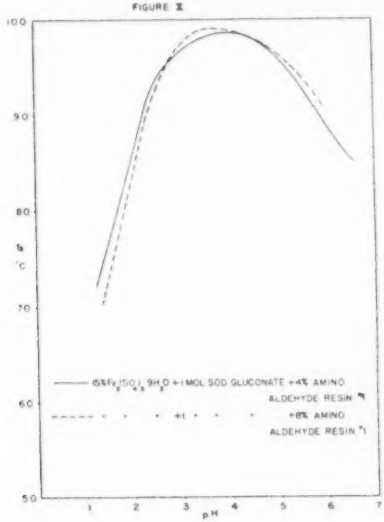


FIGURE XI

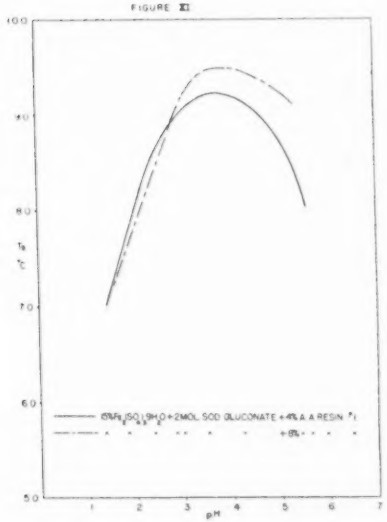


FIGURE XII

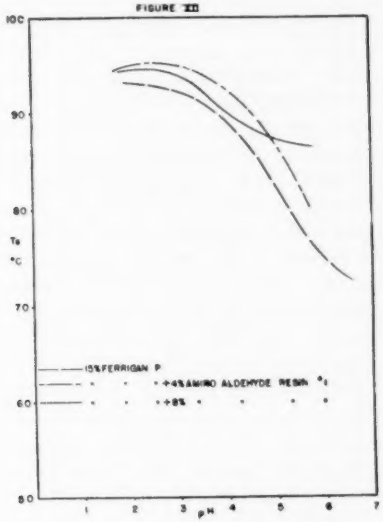
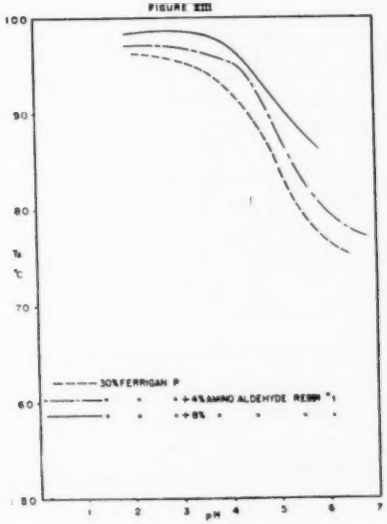


FIGURE XIII



from 80°C. to 83°C. The use of 8 per cent Resin raises the maximum Ts to 98°C., and at pH 5.5 to 88°C.

The experimental results obtained by the use of the Amino-Aldehyde Resin No. 1 allow some interesting observations:

1. With ferric sulfate alone, and with the formate ferric sulfate complex (1:1 mol ratio), the Ts gradually increased as the neutralization was continued, and at pH 5.5 the Ts's were 81°C. and 79°C. respectively.

2. The citrate ferric sulfate complex salts reacted in the same pattern as the gluconate ferric sulfate complex salts, excepting the 2 mols sodium gluconate per mol ferric sulfate salt, in that a maximum Ts was obtained and further neutralization to pH 5.5 decreased the Ts, but not to the same extent as when the Amino-Aldehyde Resin No. 1 was not used.

3. The leathers tanned with combinations of the Resin and Ferrigan P behaved similarly to gluconate leathers but were not so resistant to detanning on neutralization.

The treatment of the collagen with the Amino-Aldehyde Resin No. 1 in the proper pH range causes reaction of the methylol groups of the Resin with the basic groups of the collagen as evidenced by the Ts of the skin prior to acidification, and lack of precipitation occurring in the tan liquor when the anionic charged ferric complex salt is added to the Resin bath.

Since the Amino-Aldehyde Resin No. 1 produces by itself a Ts of 81°C. in that high pH range where drastic detanning occurs, the use of the Resin will tend to improve the Ts's or flatten out the curve obtained with those iron salts which do not produce a substantially higher Ts than 81°C. at any stage.

The influence of the Amino-Aldehyde Resin No. 1 to stabilize the Ts on neutralization can not be only the result of the tanning action of the methylol groups. If it were, the Amino-Aldehyde Resin No. 1 Ferrigan P leathers should be stabilized to the same extent as the Amino-Aldehyde Resin No. 1 gluconate ferric sulfate complex stabilized leathers.

In establishing the improved affinity mechanism imparted by the Amino-Aldehyde Resin No. 1, it is essential that the correct balance be maintained between the amount of reactive basic groups of the Resin and the negatively charged radicals of the complex salt. While excess of the Resin will have no deleterious effect on the Ts of the leather, an excess of the complex forming salt will decrease the tanning efficacy.

Conclusions Covering Primary Tannage

Leather having a high Ts can be obtained with both the gluconate and the sulfo-phthalate ferric sulfate complex salts.

The Ts of the leather tanned with either the gluconate or sulfo-phthalate ferric sulfate complex salt will decrease on neutralization to pH 5.5–6.0 by 15–20°C.

The use of a specially designed amino-aldehyde resinous material, prior to the application of the complex iron salts will, in the case of the hydroxy carboxy acid ferric sulfate complex salts, decrease appreciably this tendency toward detanning on neutralization beyond the pH at which the maximum Ts is obtained. Inasmuch as a gluconate sulfate salt produces the highest Ts among this group of acids, it is preferred. The use of this resin does not improve to any such extent the resistance of the sulfo-phthalate ferric sulfate complex salt in this respect. A balance between the amount of resin and the acid radical of the complex ferric sulfate salt is required for optimum tanning efficacy. The amino-aldehyde resin used for this purpose should be water soluble and infinitely dilutable, and capable of combining with collagen; it should be strongly cationic and should not polymerize readily to a larger molecular weight compound upon the addition of acids or acid metal salts.

Retannage for Stuffed and Fatliquored Leathers

It is conventional in the production of Army Retan to split and shave after the primary chrome tannage, then to retan with large amounts of vegetable tannins for uniformity, fullness, increased capacity to absorb stuffing greases, etc. Even if it were desired, the use of iron salts for tanning automatically precludes the possibility of performing the retanning operation with vegetable or phenolic exchange tannins. Thus it was necessary to develop a retanning agent which would exhibit the desirable properties of the vegetable tannins, particularly the plumping effect and the grease absorbing capacity. In this search we turned once again to the group of amino-aldehyde resins. Their use for this purpose requires that certain specific fundamentals be considered. The product should be water soluble; it should have affinity for tanned leather; it should be capable of being readily converted from a water soluble to a water insoluble compound, and this conversion should preferably not be a polymerization process.

The amino-aldehyde resins as such fall short of meeting these specifications in that the reactivity of the methylol groups cannot be utilized since the pH of the leather cannot be raised to the required range for chemical combination without causing deleterious effects on the leather. Without this chemical affinity, the best which might be accomplished would be a more precipitating or pigmenting effect. Hence the problem was to introduce a bridging group to provide chemical affinity between the resin and the tanned leather. We have developed such a product by means of introducing a sulfonic group into the amino-aldehyde resin. Such a resin is now being produced on a commercial scale and will be called Amino-Aldehyde Resin No. 2.* This product meets all of the above stated requirements.

The application of this material on mineral tanned stock produces the same results as are obtained with vegetable tannins in regard to chemical

*Chemtan R-6

affinity, filling action and grease absorbing capacity. Furthermore, the resin is non-astringent in that even large amounts produce extremely smooth leather which also is very strong.

The formulations for the production of stuffed army retan leather and fat-liquored side upper leather are the following:

The primary tannage for both types is identical.

Primary Tannage

All percentages are based on the unsplit, lime fleshed weight.

Wash, bate and delime completely.

Wash 30 minutes at 75°F. and drain.

Add 50 per cent water at 75°F.

Add 4 per cent Amino Aldehyde Resin No. 1 in 35 per cent water at 75°F. in three additions, 15 minutes apart, and drum 4½ hours after the last addition.

Add 5 per cent NaCl dry and drum 10 minutes.

Add 1.75 per cent H_2SO_4 in 15 per cent water at 80°F. and drum 30 minutes.

Add Iron Tanning Salt, using the equivalent of 10 per cent $Fe_2(SO_4)_3.9\ H_2O$. See directions for preparing the Iron Tanning Salt.

Drum 5 hours.

Add 1.5 per cent sodium bicarbonate in 25 per cent cold water in 2 additions, 15 minutes apart, and drum 60 minutes after the last addition.

Horse up.

Retannage—Stuffed Leather

Wring, set out, split and shave to desired weight.

All percentages based on the shaved weight.

Sides in drum.

Add 150 per cent water at 120°F. and 5 per cent NaCl, and drum 10 minutes.

Add Iron Tanning Salt, using the equivalent of 5 per cent $Fe_2(SO_4)_3.9\ H_2O$, and drum 2 hours.

Add 0.75 per cent sodium bicarbonate in 15 per cent cold water in 2 additions, 15 minutes apart, and drum 20 minutes.

Drain liquor and add 25 per cent sodium acetate in 100 per cent water at 85°F, and drum 20 minutes.

Wash 5 minutes at 120°F. and drain.

Add 100 per cent water at 140°F.

Add 10 per cent Amino-Aldehyde Resin No. 2 dry and drum 10 minutes.

Add 3 per cent boric acid dry and drum 2 hours.

Add 5 per cent $Al_2(SO_4)_3.18\ H_2O$ in 40 per cent water at 80°F. in 3 additions, 10 minutes apart, and drum 30 minutes after the last addition.

Horse up and prepare for stuffing.

Retannage—Fatliquored Leather

Wring, set out, split and shave to desired weight.

All percentages based on the shaved weight.

Add 150 per cent water at 120°F. and drum for 20 minutes and drain.

Add 80 per cent water at 140°F.

Add 3 per cent Amino-Aldehyde Resin No. 2 dry and drum 45 minutes.

Add Iron Tanning Salt, using the equivalent of 5 per cent $Fe_2(SO_4)_3.9\ H_2O$, and drum 2 hours.

Add 0.5 per cent sodium bicarbonate in 15 per cent water at 80°F. in 2 additions, 10 minutes apart, and drum 20 minutes after the last addition.

Drain and add 2 per cent sodium acetate in 100 per cent water at 85°F., and drum for 20 minutes.

Wash 5 minutes at 120°F. and drain. Fatliquor.

Preparation of the Iron Tanning Salt

One mol ferric sulfate ($Fe_2(SO_4)_3.9\ H_2O$) is dissolved in water at 95–100°C. with agitation. One mol gluconic acid is added. The solution is cooled to 35°C. and made 33 per cent basic by the addition of a sodium carbonate solution with agitation. The liquor is then diluted with cold water to a 25 per cent solution, based on the amount of ferric sulfate.

Figure XIV demonstrates the stratigraphic analysis of the stuffed army retan upper side leather made with the process as described.

FIGURE XIV

Iron Resin Tanned Leather

Weight Fraction	21.3	34.0	44.8	69.2	85.8	100	
Layer No. Grains	1	2	3	4	5	6	Composite
Moisture	6.57	5.90	5.78	5.50	7.01	6.48	6.55
Ash	8.09	7.72	7.83	7.97	7.94	8.39	7.93
Fat	29.87	20.40	14.83	12.37	14.00	18.01	18.75
Hide Substance	52.30	59.50	64.40	64.50	66.80	66.10	58.15
Iron as Fe_2O_3	6.99	6.72	6.80	6.55	6.29	6.56	6.50
pH							3.9

Overall Conclusion

Large scale tanning tests have demonstrated that by means of a tannage involving certain amino-aldehyde resins and a gluconic acid ferric sulfate complex salt, a satisfactory replacement can be produced for the conventional chrome tanned - vegetable retanned army upper side leathers.

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Bibliography

1. Ruppenthal, K. F. and Malik, J. P., *Shoe and Leather Reporter* **228**, No's. 3, 7, 12 and 19 (1943) abstracted at length *J. Amer. Lea. Chem. Asso.*, **38**, 148 (1943).
2. Thorstensen, T. C. and Theis, E. R., *J. Amer. Lea. Chem. Asso.*, **44**, 841 (1949).

Discussion

W. O. Dawson: I would like to divide the basic tannage into two classes for heavy unsplit leathers and for lighter leathers—doeskin, calfskin, possibly sheepskin. Since we thought there might be some differences, we had been very slow in trying to go from heavier over to lighter leather. Within the last two or three weeks a test was made on calfskins and the results indicated that on the four first tests the same findings as we obtained on the unsplit or heavier leathers. That test has not been completely finished. One skin was pushed ahead. This was a fat liquored leather. I can say that, so far, it appears to be working perfectly all right and at least in line with our other findings on heavier leathers.

A. N. Kay: Mr. Dawson, was there a little problem in connection with vegetable retanning regarding color and so on?

Mr. Dawson: If I interpret your question correctly, the answer is this: In the first place, we cannot use vegetable or phenolic exchange tans for retanning iron leather, which necessitated the development of resinous materials which could be used for retanning this leather and which would give essentially the same characteristics as vegetable extracts on chrome leather.

We know that the fat liquoring phase has to be different from the normal method of fat liquoring. Therefore, the coloring also would require a different system. At least that is what I expected. The result actually in this one particular case was that it colored exactly the same with this method as with normal method. The results were the same. I do not mean to imply that will be true all the time, because it may not be.

L. Seligsberger: As regards choice of hydroxyl carboxylic acid, which are possible to use?

Dawson: In our opinion, the two acids that we are most interested in are citric and gluconic. Saccarhic and mucic are not available in large quantity at all. It is a choice of the citric or gluconic. The lack of availability of citric acid in relation to the amount necessary to be used in tanning makes gluconic acid definitely the better material to use in practically every respect, economically speaking also.

Channon: Is there any explanation as to why with iron salts more organic augmenting agents are required than with the chrome? Those of us who have worked in that field have found that certain organic elements called buffers or antigens are required. Why does it require more of these organics in iron tannages as compared with chrome tannages? Are you in a position to voice an explanation?

Dawson: No, I do not think I am. I think it is a mistake to compare the chromium salts and ferric sulphate and assume them to be so similar that you should have the same effect when you add these various materials.

CHANNON: We amplify in the case of iron salts with more organics.

CHAIRMAN: Do you not think, Mr. Channon, that it is a question of type of complexes? When you add alkali to iron or chromium salt solutions, you have an entirely different effect on the particular complex.

In other words, addition of alkali to a chromium salt with chromium you really bring about a 33 or 66 per cent complex, but with iron salt you really precipitate as iron hydroxide unless particlar stabilizing salts are used. For instance, we know from our own laboratory work that formate is a fine material for chroming but has no value for aluminum or iron salts. The higher molecular weight material such as gluconic acid is about the finest one you can use in stabilizing the iron but is not satisfactory for the chrome salt.

CHANNON: I agree with your outline, but it seems to me there is a relationship there. We do not have much organic split. We do get into organics or complexes in chrome tanning, and in most iron tannages we amplify the organic conditions. My question is whether there is at this time an explanation as to why in the case of iron tannages we have to use more organic factors.

DAWSON: The one thing all of the work has pointed to is that we are forgetting the use of an amino aldehyde resin. The ferric salt by itself does not give tanning effect. In order to obtain a tanning effect with ferric sulphate, all the experimental evidence indicates that you have to have organic acids containing hydroxyl groups as a complex former. There are limits to that, and it is dependent upon the individual acid you use.

MR. HOLLOWAY: I should like to ask if in your preliminary work you investigated phosphates.

DAWSON: We had completed quite a bit of work on that particular phase prior to this. I did not report it simply because in everything that I have done I have not been successful in getting what I would call a good piece of leather with the phosphate ferric complex salts.

MR. TU: I am rather inclined to think that there is a difference between the treated oxide, between ferric and chromium, and therefore the acid is stable. It probably requires more organic hydroxyl to stabilize it.

R. M. KOPPENHOEFER: I had not associated the cationic as being a substitute with collagen. I should like to know if you have evidence to indicate that amino aldehyde functions more to that effect.

DAWSON: I think the evidence that we have indicates that; after the treatment with the amino aldehyde resin, the leather is resistant to shrinking at 81 degrees centigrade. You have a shrinkage resistance of the untanned stock after the application of the amino aldehyde resin that is as high as that of vegetable tanned leathers.

The Chemistry of Vegetable Tannins

II Quebracho

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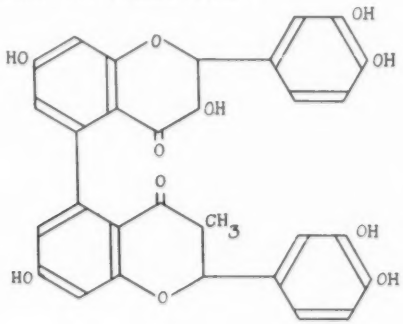
In an earlier article[1] certain experimental data were presented leading to development of an empirical formula for the main constituent of quebracho tannin. These results may be briefly recapitulated:

A. Probable basic formula: $C_{31}H_{28}O_{11}$
B. Formula for the methylated derivative: $C_{31}H_{21}O_4(OCH_3)_7$
C. Formula for the demethylated derivative: $C_{31}H_{22}O_5(OCH_3)_6 \cdot H_2O$
D. Formula for the acetyl derivative: $C_{31}H_{17}(O\,Ac)_{11}$
E. Formula for the deacetylated derivative: $C_{31}H_{23}O_8(O\,Ac)_3$
F. Formula for the methylated and acetylated derivative: $C_{31}H_{14}O_2(OCH_3)_7(O\,Ac)_2$
G. Veratric acid obtained by degradation of the methylated derivative.
H. Resorcinol obtained by degradation of the extract.
I. One terminal methyl group found present in the extract.
J. Methylated and acetylated derivatives found to be optically active.
K. Certain intermediate breakdown products obtained by oxidation, fusion and nitration.

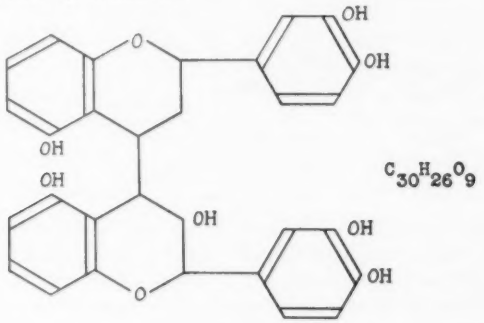
It is the purpose of this paper to discuss the relationship of various possible structures to the observed data. In order to devise a possible formula, we must arrange initially to provide for the degradation of the substance to resorcinol and protocatechuic acid. A minimum of seven hydroxyl groups are required to explain the formation of the heptamethyl derivative. We may postulate the presence of keto groups to explain the carbonyl absorption.

Let us consider the formula below:



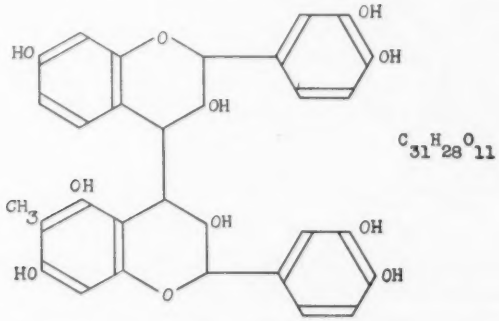
$C_{31}H_{24}O_{11}$

Methylation of the above would give a heptamethyl derivative as found. Reductive acetylation with opening of the flavanone rings to the chalcone form as is known to occur in base would give the undecacetyl derivative as found. However, acetylation without reduction gave the same result; whereas, the structure suggested would only yield an enneacetyl derivative. The formula lacks four hydrogen atoms. It does not indicate three hydroxyl groups as being different from the others as indicated by the deacetylated product. Thus, it fails in several aspects to explain the observed data. Furthermore, the actual keto absorption found in the infra-red spectrum is much less than is given by a single keto group. Let us consider the following formula suggested by Williams[2]:



$C_{30}H_{26}O_9$

It does not have the desired elementary analysis, lacks a terminal methyl group and does not account for the production of 3, 5 dinitro 2, 4 dihydroxy benzoic acid[3]. By making certain changes these requirements can be fulfilled, viz.:

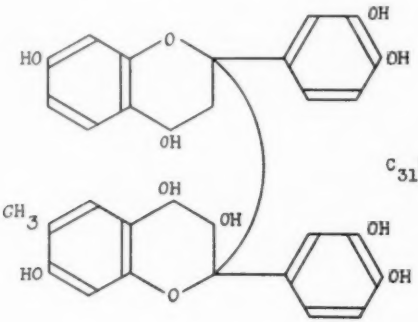


$C_{31}H_{28}O_{11}$

The structure, however, fails to account for the three hydroxyl groups which the deacetylated derivative indicates are probably aliphatic. The loss

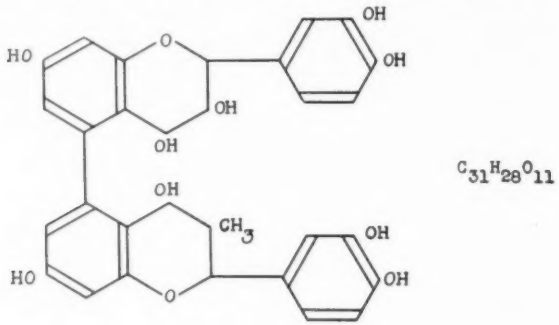
of a single methyl group by demethylation is unexplained. Although it is possible to form a model of the suggested structure, the hydroxyl groups are greatly crowded and rotation about the bond joining the two halves of the molecule is not possible.

Let us consider that possibly the two halves of the molecule may be joined as shown:



This linkage has been shown to exist in the reduction product of chalcone by Finch and White[4]. A model of this shows that only one stereoisomeric form having all the aliphatic hydroxyl groups in a given position is sterically possible and that this structure has practically no freedom of movement.

The structure preferred at present by the author is that shown below:



This structure can account for the acetylated and deacetylated products since ring opening should give the undecacetyl derivative, and deacetylation to the triacetyl compound would be expected to leave the three acetyl groups on the aliphatic hydroxyl groups. The hydroxyl group in the odd position can account for the seventh methyl group in the heptamethyl derivative and

could also be the position from which one methyl group is removed in demethylation. The addition of two acetyl groups to the heptamethyl compound can be explained by reaction with the two remaining aliphatic hydroxyl groups.

The small amount of keto absorption in the original extract may be due to a portion of the compound having one pyran ring open with resultant ketonisation of the enol.

An acetyl analysis of purified quebracho (A) by alkaline hydrolysis gave an acetyl content of 8.83 per cent, whereas acid hydrolysis gave none. It has been shown[5] that certain methyl pyrones yield acetic acid on treatment with alkali. The decomposition of the pyran rings is probably the source of the acetic acid. The infra-red spectrogram indicates the presence of a very much smaller keto absorption than would be expected if one acetyl group were actually present as such. It is, therefore, assumed to be absent.

The calculated amount of acetyl for one acetyl group is 7.24 per cent. The question then arises, if there is only one terminal methyl group, how can the acetyl content exceed the value for one group. The answer lies in the fact that compounds of this type when analyzed by alkaline hydrolysis for acetyl content give an acetyl value even though no terminal methyl group is present. For example, a sample of d-catechin when analyzed gave a value of 7.87 per cent acetyl. Since there are two pyran rings presumed to be present in quebracho, the excess acetic acid could have come from the other ring.

The preferred structure indicates more than is actually known at the moment. If the substance actually consists of two similar halves, the mode and position of the linkage has not yet been determined. The actual positions of the methyl and aliphatic hydroxyl groups are unknown. In a subsequent paper certain intermediate breakdown products whose probable structures may be related to the preferred structure of quebracho will be discussed.

Bibliography

1. Putnam and Gensler, *J. Am. Leather Chemists' Assoc.*, **46**, 613 (1951).
2. Williams, Technical Bulletin of the Leather Ind. Research Inst., S. Africa No. 35 (1947).
3. Einbeck and Jablonski, *Ber.*, **314**, 1906 (1923).
4. Finch and White, *J. Chem. Soc.*, P. 3367 (1950).
5. Späth and Gruber, *Ber.*, **71**, 106 (1930).

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The Chemistry of Vegetable Tannins

III. Wattle*

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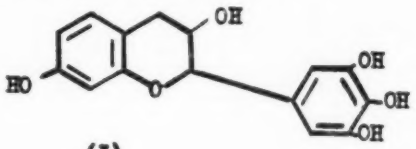
The analyses of wattle tannin and several of its derivatives listed in Table I have been abstracted from a publication by Roux.[1]. On the basis of these and other data Roux suggests that wattle may be represented as a combination of five or six $C_{15}H_{14}O_6$ units linked by the elimination of hydrogen between the hydroxyl group of one unit and the aromatic ring of an adjacent unit, and that the most probable structure for the $C_{15}H_{14}O_6$ unit is that of 3, 7, 3′, 4′, 5′–pentahydroxy–2–phenylchromane (I).



(I)

The purpose of the present paper is to call attention to a relation between quebracho and wattle tannins which has bearing on the problem of the structure of these compounds.

TABLE I

Experimental Analytical Values for Wattle and its Derivatives as Reported by Roux (1).

Material	C	H	Methoxyl	Acetyl
Wattle tannin (a)	60.90–61.04	4.83–4.94	.....	.....
Wattle tannin (b)	61.6, 61.7	4.53, 4.61	.....	.....
Wattle tannin (c)	61.38, 61.80	4.69, 4.84	.....	.....
Methylated wattle (d)	65.87 (av.)	6.16 (av.)	36.47	.....
Acetylated methylated wattle (e)	.....	.....	34.55	3.56
Acetylated methylated wattle (f)	.....	.....	34.3	4.0
Acetylated wattle (g)	58.4–58.7	4.6–4.7	.....	38.1–41.3
Acetylated wattle (h)	59.99 (av.)	4.73 (av.)	.....	37.73 (av.)

Notes. (a) Earlier work. (b) As reported by Corbett. (c) Combustion under slight pressure. (d) Methylated wattle tannin remethylated and chromatographed five times. (e) Methylated tannin as in (d) acetylated with acetyl chloride and pyridine. (f) Methylated tannin acetylated with acetic anhyxride and sodium acetate as reported by Stephen. (g) Earlier work. (h) Tannin carried through two acetyl chloride-pyridine treatments and two chromatographic purifications.

*Abstracted from a portion of the thesis of Robert C. Putnam presented in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Boston University.

**We wish to express our appreciation and thanks to the United Shoe Machinery Corporation, Research Division, Beverly, Massachusetts for defraying much of the expense incurred during this study, and for making its laboratories and other research facilities available for our use.

In our earlier work on quebracho tannin, acetylation conditions were found under which peracetylation occurred, and which permitted conversion of quebracho ($C_{13}H_{24}O_{11}$) to peracetyl quebracho ($C_{31}H_{17}(OCOCH_3)_{11}$ [2]. Application of the same acetylation procedure to wattle resulted in an analogous conversion. The analytical results (Table II.) were in agreement with the formulation of the peracetylated wattle as $C_{30}H_{14}(OCOCH_3)_{12}$, and suggested the formulation $C_{30}H_{26}O_{12}$* for wattle itself.

TABLE II

Experimental Analytical Data for Peracetylated Wattle and the Tannin.

Material	C	H	Methoxyl	Acetyl
Partially purified wattle tannin	59.9, 60.1	5.2, 5.1	1.2, 1.3	.....
Peracetylated wattle	59.90, 60.18	4.48, 4.18	.....	47.35, 48.66

Actually, comparison of the values in Table III, which was compiled on the basis of this formulation, with the experimental data given in Tables I and II shows a reasonable correspondence, and lends support to this possibility.

TABLE III

Calculated Analytical Values for Wattle and its Derivatives on the Basis of a $C_{30}H_{26}O_{12}$ Formulation.

Material	Molecular Formula	C	H	Methoxyl	Acetyl
Wattle	$C_{30}H_{26}O_{12}$	62.29	4.50	....	....
Wattle	$C_{30}H_{26}O_{12}$. 0.5 H_2O	61.33	4.63	....	....
Wattle	$C_{30}H_{26}O_{12}$. 1.5 H_2O	59.5	4.8	....	....
Methylated wattle	$C_{30}H_{18}O_4(OCH_3)_8$	66.09	6.10	35.9	....
Acetylated methylated wattle	$C_{30}H_{17}O_3$ $(OCH_3)_8$ $(OCOCH_3)$	....	....	33.9	5.9
Acetylated wattle	$C_{30}H_{18}O_4(OCOCH_3)_8$	60.39	4.63	....	37.6
Peracetylated wattle	$C_{30}H_{14}(OCOCH_3)_{12}$	59.89	4.65	....	47.69

The available molecular weight measurements are not all accommodated by the $C_{30}H_{26}O_{12}$ formulation. In the present work satisfactory agreement was obtained between the molecular weight calculated for the peracetyl derivative as $C_{30}H_{14}(OCOCH_3)_{12}$ and the value found in Rast determinations (1083 vs. 926 and 926). However, the values mentioned by Roux [1] for the

*Roux actually examines and compares two formulations, $C_{15}H_{14}O_6$ and $C_{15}H_{12}O_6$, for his basic unit. However, in the comparisons, evidently these formulations are treated more as empirical formulas than as formulas representing the actual number of atoms in the unit. It will be noted that doubling the $C_{15}H_{12}O_6$ unit of Roux results in the $C_{30}H_{26}O_{12}$ formula now to be considered.

tannin, the methylated derivative, and the (partially) acetylated derivative are not in good agreement with corresponding values calculated on the basis of the $C_{30}H_{26}O_{12}$ formulation (i. e. 1570–1760; 1700 av. and 1950 max.; and 1300–3000 av. and 1450–3500 max. as compared to 578, 690, and 914, respectively). Only further experimentation can resolve the discrepancies.

If we accept the $C_{21}H_{25}O_{11}$ formula for quebracho [2] and the $C_{30}H_{26}O_{12}$ formula for wattle, it will be seen that the former expression has one more methylene group and one less oxygen atom than the latter. Structurally, this difference may be interpreted by considering quebracho as having a methyl group which is lacking in wattle, and by considering wattle as having an extra hydroxyl group which is lacking in quebracho. These structural expressions for the difference in molecular formulas find support in the observations that although no C-methyl grouping is present in wattle [1] there is evidence for one such grouping in quebracho [2]; that whereas methylated wattle furnishes both 3,4-dimethoxybenzoic acid and 3,4,5-trimethoxybenzoic acid on oxidation [1], only the former acid* is obtained from methylated quebracho [2, 3]; and that the peracetyl derivatives of quebracho and wattle have, respectively, eleven and twelve acetyl residues.

The general similarity in behavior as well as the relations brought out above suggest that quebracho and wattle tannins may be closely related in structure. As to what these structures actually are, we feel that, taking all the available data into account, no proposal made to date serves as a completely adequate or unique expression for either of these tannins.

Experimental Section

1. Wattle Purification

Dry African black wattle extract was purified by rotating the following mixture overnight in a bottle: [4]

60 g. Extract
60 cc. Water
30 cc. Alcohol
90 cc. Acetone
360 cc. Ethyl acetate

The layers were separated and the solvent layer evaporated to dryness in vacuo on a water bath. The residue was ground. It weighed 28 g. It was mixed with methyl ethyl ketone at room temperature. A portion dissolved. The undissolved part was collected by filtration and dissolved in hot methyl ethyl ketone. A small portion failed to dissolve. This was filtered off. The filtrate was poured into ether with stirring. The precipitate which appeared was collected, washed with ether and allowed to dry in air. The product

*It is suggested that the *free* gallic acid present in quebracho [White, J. Soc. Leather Trades' Chemists, **33**, 39 (1949)] is the source of the gallic acid isolated by Perkins and Gunnell (J. Chem. Soc., **69**, 1303 (1896).)

was cream-white in color and weighed 18.5 g. It was dried two hours in a pistol at 125°C. It started to darken at 185°C. but did not have a melting point. The product was not as pure as might be desired and no doubt further treatment would significantly reduce the methoxyl content. Due to lack of time, it was used as prepared and found satisfactory for acetylation.

Analysis of the partially purified wattle:

Calc.	$C_{30}H_{26}O_{12} - 1.5\ H_2O$		
	C 59.5	H 4.8	
Found	C 59.9	H 5.2	MeO 1.2
	60.1	5.1	1.3

2. Acetylation of Wattle

The purified wattle extract was acetylated twice in precisely the same manner as the quebracho extract [2] and purified with exactly the same solvents. Five grams of extract gave 2.5 g. product. It sintered at 180°C. A third acetylation was performed by repeating the acetic anhydride treatment. One-half gram gave 0.3 g. white product sintering at 165°C. but having no clear melting point. Rast molecular weight determinations gave a value of 926. Some decomposition occurred during the measurement as evidenced by a gradual darkening of the mixture:

Calc.	$C_{30}H_{14}$ (O Ac.)$_{12}$			
	C 59.89	H 4.65	Ac 47.69	M.W. 1083
Found	C 59.90	H 4.48	Ac 47.35	M.W. 926
	60.18	4.18	48.66	926

References

1. Roux, *J. Soc. Leather Trades' Chemists*, **34**, 129 (1950).
2. Putnam and Gensler, *J. Am. Leather Chemists Assoc.*, **46**, 613 (1951).
3. Freudenberg and Maitland, *Ann.*, **510**, 193 (1934).
4. Buchanan, Lewis and Weber, *J. Am. Leather Chemists Assoc.*, **45**, 513 (1950).

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The Analysis and Chemical Composition of Naphthalene Sulfonic Acid Syntans

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Introduction

The analysis of naphthalene syntans prepared by condensation of naphthalene sulfonic acids with formaldehyde has been described by Wolesensky [1]. In order to determine their chemical composition by his procedure it is necessary to determine the acidity, total sulfur, and total inorganic matter (sulfated ash). Determination of the total sulfur by the procedures outlined by Wolesensky [1] or by use of the Parr Bomb is time consuming.

Recently we have found that the chemical composition of naphthalene syntans can be determined by measuring the acidity, the total ammonia or alkali metals and the amount of lead equivalent to the sulfate present by means of the polarograph. The method has been found to be both accurate and rapid.

The sulfated ash procedure cannot be applied directly in the case of syntans which have been neutralized partially or completely with ammonia. Therefore, it has been found expedient by us to determine the nitrogen or ammonia by caustic distillation into standard acid. However, this procedure, although satisfactory, presents a serious drawback in that foaming may occur during distillation. A direct procedure for the determination of nitrogen has been reported by Kolthoff and Stenger [2] using calcium hypochlorite. This procedure has been applied by us to naphthalene syntans either wholly or partially neutralized with ammonia and has been found to yield results in good agreement with those found by caustic distillation.

The determinations outlined above yield data which are related only to the sulfur constituents, i. e., total sulfur, sulfates (acid and neutral) and combined sulfur. In order to obtain additional information concerning the composition of the syntan several assumptions can be made on the basis of theoretical considerations as follows:

1. When the degree of sulfonation is equivalent to one mole of combined acid per mole of naphthalene or less no disulfonation occurred.

2. When the degree of sulfonation is equivalent to more than one mole of combined acid per mole of naphthalene mono- and disulfonated naphthalene is present.

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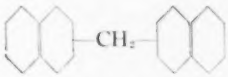
‡**Present address Tannin Extract Division, The Mead Corporation, Lynchburg, Virginia.

In our calculations we assume that two molecules of naphthalene, either sulfonated or not, are linked by one molecule of formaldehyde during condensation as shown below:



This assumption is made since we have no readily available means at present of determining the naphthalene and methylene groups present nor of separating constituents into molecular fractions.

If the non-volatile matter is determined as described by Wolesensky [1] or calculated from the loss determined by drying a neutralized sample at 100° –

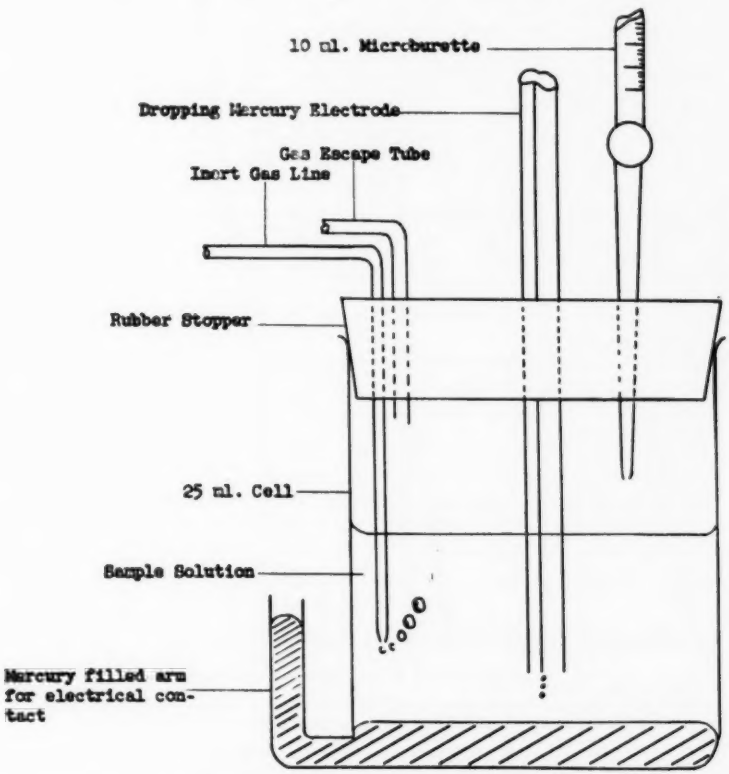


FIGURE 1—Cell Used for Amperometric Titration of Sulfate with Lead Nitrate

105°C. then the organic matter may be calculated by subtraction of the neutral and acid constituents. The organic matter obtained in this manner is represented as described above, i. e., methylene-bis-naphthalene, and is used in calculating so-called "strength units".

The strength unit serves as a measure of the quantity of "active ingredient", methylene-bis(naphthalenesulfonic acid), present. One strength unit is equivalent to 0.18 per cent of methylene-bis(naphthalenesulfonic acid) or in terms of naphthalene to 0.107 grams or 0.00841 millimoles of naphthalene per gram of syntan.

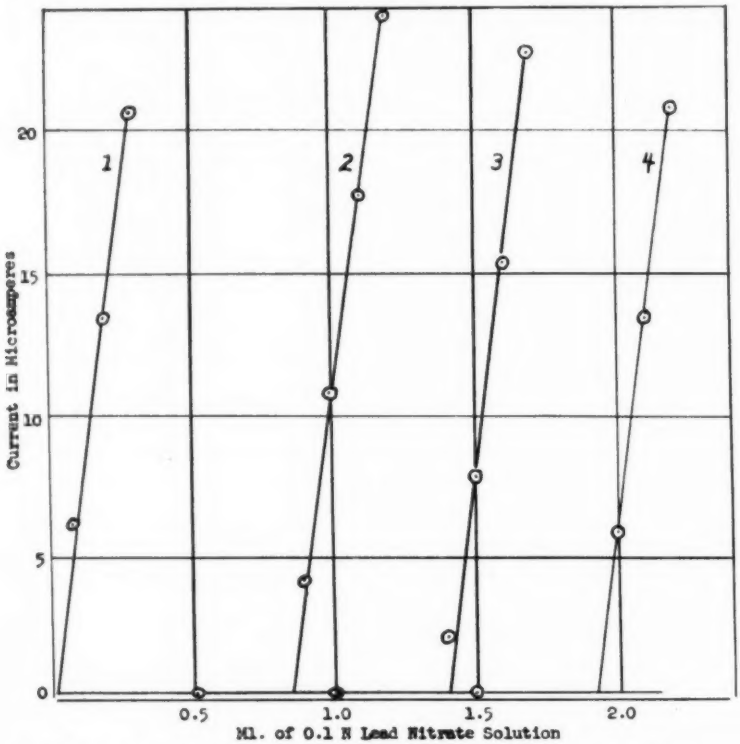


FIGURE 2—Typical Lead Nitrate Titration Curves of a Sulfate Free Naphthalene Syntan Containing Known Amounts of Added Sulfate.

Curve 1— 0.00 milligrams added Sodium Sulfate
Curve 2— 7.38 milligrams added Sodium Sulfate
Curve 3—10.20 milligrams added Sodium Sulfate
Curve 4—13.64 milligrams added Sodium Sulfate

PART I

The Analysis Of Naphthalene Syntans

When lead nitrate is added to a sulfate containing solution, lead sulfate precipitates. After the endpoint is reached the excess lead ions are determined amperometrically using the polarograph. Accuracy and sensitivity of this procedure has been demonstrated [3]. We have found that naphthalene syntans do not interfere in the determination.

The amperometric titration of the sulfates present in naphthalene syntans was carried out in a cell as illustrated in Figure 1. The cell size was about 25 ml. and was fitted with a nitrogen bubbling tube, a microburette containing 0.1N lead nitrate, a dropping mercury electrode and a mercury pool. When the lead nitrate is added to the solution in the cell containing sulfate, lead sulfate precipitates. In order to render the lead sulfate more insoluble, 60 per cent ethanol is used as a medium. At an applied potential of –0.7 volt no current is registered until an excess of lead has been added. The endpoint is found graphically as the point of intersection of the "residual current" line before the endpoint and of the cathodic current line (at –0.7 volt) of lead after the endpoint. By measuring the current after adding successive amounts of lead nitrate solution and obtaining two or more values in the presence of an excess of lead the endpoint is found by graphical extrapolation to the residual current line. The volume of the lead solution at this point is equal to that at the equivalence point. Typical titrations are shown in Figure 2.

The amperometric method for sulfate determination was tested by adding known amounts of sodium sulfate to sulfate-free samples of naphthalene-sulfonic acid, naphthalene-sodium sulfonate and a commercialn aphthalene syntan from which sulfate had been removed. The sodium sulfate used was reagent grade and dried before using. The sulfate-free materials were made by dissolving the dried neutral sulfonates in ethanol and filtering. The sulfonates are soluble while the sodium sulfate is insoluble in ethanol and is filtered off. Naphthalene sulfonic acid was made by acidifying the sodium sulfonate. Experimental values for the determination of sulfate by this method are given in Table I.

The recommended reagents and analytical procedures for determining the composition of naphthalene syntans are as follows:

Reagents:

1. Distilled Water
2. 0.1 N Sodium Hydroxide Solution
3. 0.1 N Lead Nitrate Solution
4. Anhydrous Ethanol
5. Saturated Potassium Chloride Solution
6. 0.1 per cent Methyl Red Indicator

7. 0.1 N Calcium Hypochlorite Solution
8. 0.1 N Sodium Arsenite Solution
9. 0.01 N Sodium Arsenite Solution
10. 10 per cent Potassium Bromide and 5 per cent Sodium Bicarbonate Solution
11. 0.2 per cent Bordeaux Red Solution

TABLE I

Amperometric Titration of Sulfate Free Naphthalene Sulfonic Acid, Naphthalene Sodium Sulfonate and a commercial Naphthalene Syntan Containing known Added Amounts of Sodium Sulfate.

	Mg. Sodium Sulfate Added	Ml. 0.1N Lead Nitrate Used	Mg. Sodium Sulfate Found	Error Per cent
Naphthalene Sulfonic Acid	00.00	0.02	00.14	–
(0.25 gram sample)	24.79	3.40	24.47	+1.2
	24.79	3.48	25.03	+1.0
	48.25	6.66	47.99	−0.5
	74.60	10.60	74.15	−0.6
Naphthalene Sodium Sulfonate	00.00	0.01	0.07	–
(0.25 gram sample)	12.39	1.66	12.28	−0.8
	24.79	3.45	24.84	+0.2
	48.25	6.71	48.44	+0.4
	74.60	10.39	74.85	+0.2
Commercial Naphthalene Syntan	0.00	0.02	0.14	–
(0.50 gram sample)	20.30	2.84	20.43	+0.6
	27.08	3.74	26.93	−0.6
	27.08	3.81	27.38	+1.1

Procedure:

1. *Sample Preparation*: Accurately weigh 10 grams of sample of approximately 150 strength units* and transfer to a 100 ml. volumetric flask. Dissolve and make up to volume with distilled water.

2. *Total Acid Determination*: Pipette 25 ml. of prepared sample into a 250 ml. Erlenmeyer flask. Add 25 ml. of distilled water and titrate against 0.1 *N* sodium hydroxide using Methyl Red indicator. Express acidity, A, as milli-equivalents per gram sample, calculated:

$$0.4 \times \text{ml.} \times \text{Normality}$$

If the sample is alkaline, titrate with 0.1 *N* HCl and express acidity, A, as a negative value, calculated:

$$0.4 \times \text{ml.} \times \text{Normality}$$

*The weight of sample of an unknown for analysis may be calculated roughly from a total solids determination on the assumption that 1.5 moles of sulfuric acid was used per mole of naphthalene in preparing the syntan. On a molar basis there would be produced theoretically 0.5 mole of the sodium salt of methylene-bis(naphthalenesulfonic acid) and 0.5 mole of sodium sulfate. If the syntan containing this mixture were so diluted that the solids were equivalent to 48.75 per cent then the strength units would be equivalent to 150.

3. *Nitrogen Determination*: Pipette 5 ml. of prepared sample into a 250 ml. Erlenmeyer flask. Add the same amount of 0.1 *N* Sodium Hydroxide as used in the Total Acid Determination. Add 10 ml. of the 10 per cent potassium bromide and 5 per cent sodium bicarbonate solution. Titrate against 0.1 *N* calcium hypochlorite solution until the color changes from faint yellow to darker yellow. One drop of hypochlorite will make the change. Add 3 drops of Bordeaux Red indicator. If decolorization is not immediate the hypochlorite addition is not complete. Care must be taken not to exceed this point by more than 0.5 ml. Allow the flask to stand for 2 minutes. Add 10 ml. of 0.01 *N* sodium arsenite solution. Add 3 drops of Bordeaux Red indicator and cautiously continue titration until 1 drop will change the color of the solution. Add 3 more drops of Bordeaux Red and continue titration dropwise until the color changes to yellow. Continue in this manner until the solution remains yellow upon the addition of Bordeaux Red. The calcium hypochlorite solution should be standardized on each day that it is used. Express Nitrogen, N, as milliequivalents per gram sample, calculated: 0.6665 x [ml. Hypochlorite x Normality - 0.1 (correction for Arsenite added)]

Standardization of Calcium Hypochlorite: Pipette 25 ml. of 0.1 *N* sodium arsenite solution into a 250 Erlenmeyer flask. Add 10 ml. of potassium bromide-sodium bicarbonate solution and titrate with the calcium hypochlorite solution until near the expected endpoint. Add 3 drops of Bordeaux Red solution and continue cautiously titrating until the color fades. Add 3 more drops of Bordeaux Red, if the color remains continue titrating until no color is noticed upon Bordeaux addition. One drop of hypochlorite will make the final color change.

Sodium Determination: When present, sodium may be determined by the sulfated ash procedure. Use 10 ml. of the sample solution and proceed in the usual manner. The sodium expressed as milliequivalents per gram sample, N_a, calculated:

$$7.04 \times \text{weight of residue}$$

4. *Unreacted Sulfate Determination*: Pipette 5 ml. of prepared sample and 10 ml. of anhydrous ethanol into the polarographic cell. Add the mercury pool and one drop of a saturated potassium chloride solution. Place the rubber stopper, dropping electrode, etc., in place and bubble nitrogen until the solution is oxygen-free. Applying a potential of –0.7 volt proceed with the amperometric titration reading the current after successive additions of 0.1 N lead nitrate solution. Plot current against ml. of lead solution as indicated Figure 2. The endpoint is the intersection as shown. Express the uncombined sulfate, S, as milliequivalents per gram, calculated:

$$2 \times \text{ml. } Pb(NO_3)_2 \times \text{Normality}$$

5. *Neutral Solid Determination*: Pipette 10 ml. of the prepared sample into an evaporating dish. Add 0.1 N sodium hydroxide equivalent to the

acidity equivalents plus the ammonia equivalents. (Acidity equivalents are negative for alkaline syntans). Evaporate to dryness on a steam bath, and then to a constant weight in a 105°C. drying oven. No correction is made for the sodium hydroxide addition. Express Neutral Solids, M, as gram solids per gram of syntan, calculated:

$$M = \text{weight of residue per gram sample}$$

The nitrogen content of three different ammonia neutralized syntans is compared using the calcium hypochlorite and caustic distillation procedures as shown in Table II. Higher values for nitrogen were obtained in all cases in which hypochlorite was used.

TABLE II

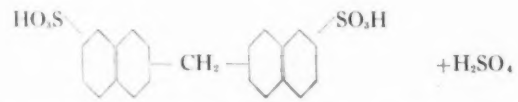
Nitrogen Content of Ammonia Neutralized Syntans Determined by Hypochlorite and Caustic Distillation

Syntan	Per cent Nitrogen	
	Hypochlorite	Caustic Distillation
1.	2.70	2.61
	2.69	
2.	1.69	1.61
	1.69	1.61
3.	2.01	1.91
	2.02	

PART II

The Composition Of Naphthalene Syntans

Basically naphthalene sulfonic acid syntans prepared by the sulfonation of naphthalene followed by condensation with formaldehyde may theoretically be considered to contain the following ingredients prior to neutralization: (1) methylene-bis(naphthalenesulfonic acid) and (2) sulfuric acid as illustrated below.



In general the combined acid varies from 0.9 to 1.1 moles per mole of naphthalene.

The products resulting from the condensation with formaldehyde may be neutralized with ammonia or caustic soda to varying degrees and diluted with water to some appropriate strength or the wholly or partially neutralized materials may be dried in order to obtain more concentrated products.

It can be appreciated that the components present in the syntan will vary depending upon the amount of alkali present. If we assume that sulfuric acid is neutralized first, then we may assume that syntans neutralized with caustic soda contain sodium sulfate, free sulfuric acid and sulfonic acids, or sodium sulfate and sulfonic acids, or sodium sulfate, neutralized sulfonic acids and free sulfonic acids or sodium sulfate and sodium sulfonates.

Basically we are interested in knowing the following with regard to the composition of naphthalene sulfonic acids syntans:

1. Sodium sulfate
2. Acidity as sulfuric acid
3. Free sulfuric acid
4. Moles of sulfuric acid combined per mole of naphthalene
5. Moles of sulfuric per mole of naphthalene
6. Strength units

The strength units are a measure of the "active ingredient" or methylene-bis(naphthalenesulfonic acid) content of the syntan.

The estimation of the constituents outlined above may be easily calculated from the determinations outlined in Part I.

In Table III are listed the determinations, calculations, and product analysis procedures for calculating the composition of naphthalene sulfonic acid syntans.

The procedures which we have outlined in this report we believe will serve to fulfill a long felt need with regard to the analysis naphthalene syntans, especially, with respect to the determination of the active ingredient content of such products.

We have found them to be useful in product control during processing as well as to measure and adjust the uniformity of finished products.

Those in the tanning industry who have had an opportunity to test our procedures have found them to be of benefit in checking the quality of products.

Summary

Procedures are outlined for determining the sulfate content of naphthalene sulfonic acid syntans by amperometric titration (polarograph). A rapid method for the determination of ammonia nitrogen is described. The composition of naphthalene sulfonic acid syntans may be readily calculated based on the analyses for either sulfates or total sulfur, sodium or nitrogen, acidity and total solids. The product analysis yields information regarding salt and acid content and more especially the "active ingredient" content in terms of strength units. This latter value is of importance when considering the application of these products industrially.

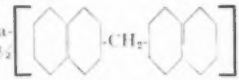
TABLE III

Procedures for Calculating the Product Composition of Naphthalene Syntans

Determinations	Report as	Symbol	Calculation
Total sulfur*	m.eq./g.	T	
Acidity	m.eq./g.	A	
Ammonia	m.eq./g.	N_1	
Sulfated ash (Na_2SO_4)	m.eq./g.	N_2	
Acid and neutral sulfates*	m.eq./g.	S	
Total solids (neutral)	g./g.	M	

*It is not necessary to determine T if S has been determined or vice versa

Calculations

Combined sulfur as sulfonate	m.mole/g.	α	T-A-N or A+N-S
Acid and neutral sulfates	m.mole/g.	β	A+N-0.5T or 0.5S
Total sulfur	m.mole/g.	γ	0.5T or A+N-0.5S or $\alpha+\beta$
Naphthalene as $\frac{1}{2}$ 	m.mole/g.	δ	$[M-0.102\alpha-0.142\beta]\frac{1000}{134}$

When solids are determined without neutralizing and acid is present or when solids are determined following neutralization but corrected for added sodium calculate as shown below:

Neutral sulfates	m.mole/g.	β_1	0.5N
Sulfuric acid	m.mole/g.	β_2	A+0.5N-0.5T or β -0.5N
Neutral sulfonates	m.mole/g.	α_1	T-2A-N or N-S
Acid sulfonates	m.mole/g.	α_2	A

When acid and neutral sulfates are present

$$\delta=\left[M-0.102\alpha-0.142\beta_1-0.098\beta_2\right]\frac{1000}{134}$$

When acid and neutral sulfonates are present

$$\delta=\left[M-0.102\alpha_1-0.08\ \alpha_2-0.142\beta\right]\frac{1000}{134}$$

Product Analysis—Report

Loss at 105°C., per cent	
Total solids, per cent	
Total sulfur as sulfuric acid, per cent	9.8γ
Sodium sulfate, per cent	$7.1\ N_2$ (1)
Ammonium sulfate, per cent	$6.6\ N_1$
Acidity as sulfuric acid, per cent	$4.9\ A$
Sulfuric acid, per cent	$9.8\beta_2$
Moles sulfuric acid combined/mole naphthalene	α/δ
Moles sulfuric acid/mole maphthalene	γ/δ
Strength units	118.9δ

NOTE: 1. When $N_2 > S$ substitute S for N_2

2. When the syntan has been neutralized with ammonia determine total solids by neutralizing sample with caustic soda to methyl red endpoint and adding caustic soda equivalent to ammonia present. Proceed with analysis and calculations making the necessary corrections and calculations.

3. The molecular weight of ammonium sulfate is 132. The ammonium sulfonate ion is 97 as one hydrogen belongs to the naphthalene ring. Total solids present in the syntan are calculated from solids determined by correcting for the sodium added.
4. Naphthalene as millimoles per gram is solved by the equation:

$$[M - 0.120\alpha - 0.142\beta]\ 1000/134$$

This equation represents a syntan composed of the sodium salt of methylene-bis (naphthalenesulfonic acid) and sodium sulfate. By subtracting the sodium sulfate (mol. wt. 142) and sodium sulfonate ($NaSO_3$ minus one hydrogen equivalent = mol. wt. 102) from the total solids, M, there is obtained the grams of methylene-bisnaphthalene (mol. wt. 268) per gram of syntan. Dividing this value by 134 and multiplying by 1000 gives the millimoles of naphthalene per gram of syntan.

5. In some instances syntans may be found in which all of the sulfonic acid constituents are unneutralized and part of the sulfuric acid is neutralized. On the other hand cases may occur in which all of the sulfuric acid is neutralized and part of the sulfonic acids are neutralized. It is assumed, as previously stated, that the sulfuric acid is neutralized prior to the sulfonic acids. When (S − N) is positive sodium sulfate and sulfuric acid are present and the sulfonic acids are unneutralized. When (N − S) is positive sodium sulfonates and sulfonic acids are present and the sulfuric acid is completely neutralized.

It will be noted in Table III that the determination of total sulfur is not necessary if sulfates have been determined by the polarograph. The illustration of the use of the value for total sulfur has been included in order to broaden the scope of the present work.

When solids are determined without neutralizing and acid is present or when solids are determined following neutralization and are corrected for added sodium use the calculations shown under neutral sulfates and sulfuric acid or neutral sulfonates and acid sulfonates as the case may be. When correcting for added sodium remember to subtract one hydrogen equivalent. The total solids, M, used in the calculations in both of the two above instances are the solids "as received", that is, determined directly or the solids obtained following neutralization but corrected for added sodium.

References

1. E. Wolesensky, *Technologic Papers of the Bureau of Standards*, **20**, No. 316, 519-527 (1926).
2. I. M. Kolthoff and V. A. Stenger, *Ind. Eng. Chem., Anal. Ed.*, **7**, 79 (1935).
3. Z. Major, *Electrochem.*, **42**, 120, 123 (1936).

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BOOK NOTICE

The Molds and Man. By C. M. Christensen. Published by the University of Minnesota Press, Minneapolis, Minn. 244 pages. Cloth, $3.00. What is your vocation, avocation or hobby? Whatever they are you are likely to find that any or all of the three are greatly affected by fungi in ways you do not suspect. Such being the case it is certainly interesting and possibly valuable to learn how. If you learn it from "The Molds and Man," you will thoroughly enjoy doing it. The book is written both for beginners and those who wish to get a general idea of the subject. For the beginner it is basic and factually accurate. For the casual reader it is a series of interesting narratives, peppered with salty humor. It seems that, lowly as they are, molds are vital in the scheme of life. Lacking chlorophyl they cannot

create food and must depend upon food already created. They literaly live to eat and eat practically everything except metals. They will even corrode the lenses of your telescope or binoculars, if the climate is favorable. Thus they are often destructive, and harmful from the human point of view. Nevertheless they are necessary for the great life cycle. Without them green plants could hardly exist and without green plants there would be no life. Diseases in plants, fish, birds, beasts and men are caused by fungi. Yet, as we all know from the stories of penicillin and streptomycin, molds also give us some of our most valuable cures. We can fight mold pests with insects and insect pests with molds. The book tells us what is known of such things, our successes and our failures. Besides giving valuable facts it exposes quite a few falsities. For example, "Save the Surface and You Save All" may be true; but it is not necessarily true that paint saves the surface. Molds both can and do live in paints and on painted surfaces. Painting cut surfaces of trees with asphalt paint may do more harm than good, and filling the cavities with cement just gives snug protection to the devouring fungi. Leather is no exception to the rule that practically everything is food for molds. A shoe or boot, after it has been worn for some time, consists partly of leather and partly of mold. So the tanner, leather chemist and shoe manufacturer may well find a bit of mycology practical as well as interesting. If so, this book is a good place to get it.

R. H. T.

ABSTRACTS

Liquid Industrial Wastes. Tanneries. By J. W. Harnly. *Ind. & Eng. Chem.*, **44**, 520 (1952). The United States Tanneries, 443 in number, produce 20 billion gallons of waste annually, concentrated geographically in 5 per cent of the country's area. One hundred eighty-three are located in nine cities, namely: Peabody, Mass.; Newark, N. J.; Salem, Mass.; Gloversville, N. Y.; Chicago, Ill.; Philadelphia, Pa.; Milwaukee, Wis.; Johnstown, N. Y., and Wilmington, Del. The author describes the work of the two A.L.C.A. Committees on tannery affluent, the first established in 1911, and the second in 1938. The work of the various state and municipal Sanitary Water Boards and River Committees is described briefly. Reference is also made to the survey made by the Tanners' Council in 1941, wherein methods of treatment were described in some detail. Work of the A.L.C.A. Committee is continuing the form of abstracting for the *Journal* all pertinent articles on the subject. An outline of the methods of waste disposal is given for tanneries located at Waukegan, Ill.; Sheboygan, Wis.; Ridgway, Pa., and Bolivar, Tenn. Waste disposal problems in areas where tanneries are concentrated, such as Johnstown and Gloversville, N. Y.; Salem and Peabody, Mass.; Chicago, Ill.; Newark, N. J., and Wilmington, Del., are discussed. The author regards the best method of disposal of tannery wastes to be its mixture with domestic sewage when an adequate volume of such sewage is available. Moreover, the disposal of tannery waste must be regarded as an integral part of plant operation, subject to as careful supervision as the other plant departments.

Waste Disposal in Britain. By B. A. Southgate. *Ind. & Eng. Chem.*, **44**, 524 (1952). Among other industries which discharge contaminating plant affluents, tanneries are included. Many of the tanneries of Great Britain discharge their waste liquors without treatment to tidal waters. Little has been done to develop methods for their purification. Among the methods applied, however, are oxidation of sulfide with chlorine, screening, and removal of suspended solids by sedimentation. Where the supply of domestic sewage is adequate, tannery affluent can be discharged to sewage disposal works.

The Color Reaction of Certain Aldehydes with Orcinol. By A. Bevenue and K. T. Williams. *Chemist Analyst*, **41**, No. 1, 5 (1952). By means of paper chromatography it is possible to differentiate between certain aromatic aldehydes, employing the following procedure: In 100 ml. of water-saturated 1-butanol dissolve 0.5 g. of orcinol and 15.0 g. of trichloracetic acid. Apply approximately 3 microliters of a 5 per cent ethanolic solution of sample to a sheet of qualitative filter paper by means of a platinum loop. Spray the paper with the orcinol reagent. Dry the paper for specified time and at definite temperatures, when colors will develop according to aldehyde and procedure. Two of the aldehydes tested were pyrocatecheuic aldehyde and vanillin.

Heat Resistant Crayons. By G. J. Kurkoski and S. Abbey. *Chemist Analyst*, **41**, No. 1, 20 (1952). Crayons suitable for marking on crucibles which are to be ignited at temperatures near 1000°C. are prepared in the following manner: Mix thoroughly 5 g. of powdered ferric oxide with 1 g. of CaO in a mortar. Add, with continuous stirring, 20 ml. of molten paraffin. Continue until a paste of uniform consistency is obtained. Mold into stick form, and wrap with paper. Marks made with such crayons on fused silica and on both glazed and unglazed porcelain will withstand repeated ignition at high temperature.

Production of Mold Protease on a Pilot Plant Scale. By M. E. Maxwell. *Tech. Paper No. 1, Wool Textile Research Lab.*, Commonwealth Scientific and Indust. Organization, Australia, 1950. See abstract of similar article *This Journ.*, **46**, 385 (1951).

Studies of the Depilatory Activity of Sodium Sulfide and Some Related Compounds. By J. M. Gillespie. *Australian J. Scientific Research B.*, **4**, 187 (1951). The depilatory action of sodium sulphide on sheepskin has been investigated by measuring the pull required to remove wool from skin, the swelling of wool root shafts, and the mechanical strength of wool. The rate of action is augmented by increase in temperature, pH value, and concentration of sulphide in the solution employed up to 1.0 M, but is reduced by increase to higher concentrations. The reciprocal action of the hydroxyl and hydrosulphide ions in digesting keratin is explained in Appendix I in terms of the ionization of sulphydryl groups. Solutions of 1.0 M sodium sulphide, partially oxidized with peroxide and adjusted to pH 12.8, completely loosen wool in 18 hours at 20°C. only if the oxidation-reduction potential is lower than—400 millivolts. Salts of various oxyacids of sulphur are less effective depilatories than sodium sulphide, the activity diminishing with increase in the number of oxygen atoms in the anion and approximately with the heat of formation. Sodium selenide and sodium telluride possess depilatory activity equal to that of sodium sulphide.

Saponification of Wool Wax and the Recovery of the Wax Alcohols. By C. S. Barnes, R. G. Curtis and H. H. Hatt, *Australian J. App. Sci.*, **3**, 88 (1952). Wool wax is rapidly and completely saponified by either sodium or potassium hydroxide in aqueous ethanol. The products are separated by extracting the wax alcohols from the wax soaps and aqueous alcoholic liquors by an immiscible solvent, such as benzene. The process is suitable for large scale operation.

Evaluation and Improvement of Leather Insoles. By S. S. Kremen. *Shoe and Lea. Reporter*, **265**, No. 7, 15 (1952). In order to produce better insoles there must first be a means for evaluating their resistance to deterioration. Two methods of evaluation can be followed, namely: the development of equipment which can well become involved and

expensive. The second approach is to establish and measure the pertinent fundamental properties of the material which are involved in the service life of the product. The author compromised between the two approaches by developing a procedure which combines flexing under pressure that the insole undergoes during walking with the alternate wetting and drying cycles of daily wear routine. The wetting material is artificial perspiration. Method of conducting the test is given in detail. Suggested procedure for improving vegetable tanned insoles are increase of oil content, decrease in water solubles and post tannage or pretannage with chrome or alum. More recent work indicates that formaldehyde post-tannage is comparable with chrome in preventing hydrolysis of the tannins and in extending the useful life of the insole. It has the additional advantage of leaving the leather undiscolored.

Pigment Finishes for Leather. By F. Welsh. *Shoe and Lea. Reporter*, **624,** No. 12, 7 (1951). The first pigment finish, made in 1890, consisted of soap, glue, sienna, umber and ochre for application on bark tanned wax splits. This was followed by the incorporation of various waxes and adhesives without, however, greatly improving the elasticity of the finish. Lakes, toners and reduced colors replaced the earth colors, new vehicles for carrying the coloring materials were developed, and various polymers and copolymers were introduced to impart elasticity to the films. The hiding power of a pigment does not necessarily depend on its concentration, since other factors, such as method of manufacture of the finish, are of great importance. Toners are pure coloring agents containing no inert matter, such as paras, toluidines and lithols. Generally paras bleed the most, and lithols the least, while toluidines are fastest to light. Lakes are made by precipitating the coloring agent on inert material, such as barium sulfate or aluminum hydroxide. Reduced colors are prepared by dry blending of a toner and an inert material. Dyes and pigments differ in that the former is soluble and is applied to leather in dissolved state, while the latter is insoluble and is applied to leather suspended in a suitable liquid vehicle. These are usually vegetable oils and glycols combined with mixtures of protein syrups, cellulose gums, silica solutions and soya proteins. In all, there are close to 100 plasticizers in use. A good pigment finish should have the following qualities: (1) Pigments should be ground to a colloid condition, at least 3 times in a wetting out medium. That will minimize sedimentation. (2) Pigments must be reasonably fast to light. (3) They shall be unaffected by alkaline solutions for a long period. (4) They shall be unaffected by heat in plating. (5) Pigments should have good covering power in comparatively weak mixture without a painted appearance. (6) The pigments should be colloidal and not granular, in order to impart a smooth, silky feel. (7) They should be unaffected by atmospheric influence. The most desirable properties of a pigment finish are uniformity, applicability, adhesiveness, flexibility, elasticity. It should have a natural feel, and should be able to withstand the various shoe making operations.

Quality Controlling Leather. By E. R. Theis. *Lea. & Shoes*, **122,** No. 22, 10 (1951). The author advocates the stratographic analysis of leather at the various stages of its manufacture. In this way the extent of tannage at any given point can be determined, the progress of neutralization ascertained, and the depth of penetration of an oil or fat liquor observed. It is felt that more accurate control of processing can be secured by this procedure.

Relations Between Elasticity and Shrinkage Temperature of Leather. By G. I. Kutyanin. *C. R. Acad. Sci., U.S.S.R.*, **85,** 299 (1949). Through *Brit. Abstr. B II*, 102 (1952). Experiments establish the direct dependence of changes in mechanical properties of hide on the hydrothermal stability of collagen after tanning, and substantiate the theory

of transverse bonds. One series of tests was carried out before tanning, the other on samples treated with various tanning materials. The high elasticities of formaldehyde-tanned leather shrunk at 90° and of chrome-tanned leather shrunk at 100° correlate well with their hydrothermal stability. Analogous conformity is shown with leather tanned by other processes. In the series of tests, measurements were made of the original thickness of the hide, its thickness under a load of 1.2 kg. per sq. cm., and after 1 hr. in a tanning solution (without compression). Thus were obtained in per cent of the original thickness the general deformation in compression, after unloading, and 1 hr. after unloading. Excepting for the raw hide 1 min. after unloading and 1 hr. after unloading, the deformation did not change. Tabulated results indicate that the general deformation, using various tanning solutions, is decreased and the elastic deformation in the wet condition is increased. The increase in elasticity corresponds to the shrinkage temperature. The direct dependence of the values for increase in elasticity on rise in shrinkage temperature establishes the theory that the increase in elasticity is due to the molecular strengthening of collagen structure by the tanning material.

Shellac Finish for Leather. By L. Angelino. *Industr. Vern.*, **5**, No. 45, 12 (1951). Through *Brit. Abstr. B II*, 102 (1952). Aqueous solutions of shellac soaps are used for leather finishes on account of their flexibility. Borax, Na_2CO_3, and aqueous NH_3 are used to bring the shellac into solution. Directions for solubilizing the resin and clarifying the solution are given. Fatty acid soaps, sulphonated oils, alginates, and glycerol are among the plasticizers suggested; notes on their use are given. Furfuraldehyde, or natural essences, in amount 1.8 per cent on the finish, are recommended as preservatives. When brushed or sponged on the leather, the finish tends to foam; this is remedied by incorporation of 2.5-3.5 per cent of H_2O-soluble organic solvents. Formulae for clear and colored finishes are given.

Effect of Tension on Water Absorption by Hair. By L. R. G. Treloar, *Nature*, **168**, 521 (1951). Through *J. Soc. Dyers and Colourists*, **68**, 44 (1952). Equilibrium moisture absorptions of horsehair under stress are measured by direct weighing, recordings being made when the stress is alternately applied and removed. There is a small, constant, and reproducible weight increase on stressing, a result in the opposite direction to that found by White and Stam (*Text. Research J.*, **19**, 136 (1949).

Free Amino Groups of Collagen. By J. H. Bowes and J. A. Moss. *Nature*, **168**, 514 (1951). Through *J. Soc. Dyers and Colourists*, **68**, 45 (1952). After heating in water at 70°C., or treating in alkali or urea, a small number of α-amino groups are found in collagen, none being detectable before treatment. Reasons for this are discussed.

Colorimetric Determination of Amino Acids by the Ninhydrin Reaction. By A. M. Smith and A. H. Agiza. *Analyst*, **76**, 623 (1951). Through *J. Soc. Dyers and Colourists*, **68**, 47 (1952). The coloured compound formed in the reaction between amino acids and ninhydrin may be used as a quantitative measure of the amino acid decomposed. The hue and depth of colour are not the same for all the common amino acids, but for individual acids there is a linear relationship between colour intensity and concentration in the range 5-25 μg. of amino nitrogen. The method is not accurate for the determination of total amino nitrogen in a mixture, but is convenient for determining the submicro quantities of amino acids obtained from a drop of protein hydrolysate fractionated by two-dimensional paper chromatography.

Identification of Free Carboxyl Groups in Peptides. By J. Tibbs, *Nature*, **168,** 910 (1951). Through *J. Soc. Dyers and Colourists*, **68,** 47 (1952). Experiments with insulin and keratin suggest that the Schlack and Kumpf procedure for identifying peptides which provide terminal carboxyl groups may have to be modified, though it has been used successfully for glycylleucine and glycylvaline. Benzoylated dipeptide is treated with ammonium thiocyanate, acetic acid, and acetic anhydride to convert to the thiohydantoin derivative; this is refluxed with 20 per cent HCl, and the hydrolysate extracted with nithromethane. After drying in vacuo and hydrolysing with $Ba(OH)_2$, excess hydroxide is removed as $BaCO_3$, and the hydrolysate examined by paper chromatography. Ninhydrin development shows only one clear spot, corresponding to the acid carrying the free carboxyl group.

Fur Improvement, also Aniline Dyes and Synthetic Fats for the Leather Industry. By D. Pense. *Oesterreichische Leder-Zeitung*, **6,** 307 (1951). A lecture discussing methods for tanning and finishing furs, leather dyes and synthetic fats. The syntan Coralon F has a bleaching action on chrome leather with the result that dyeing is more even if it is used. Coralon GA has less bleaching action but promotes even dyeing and a "full" leather; from 0.5 to 2% may be used before, during or after dyeing. Derminol oil is stable and imparts mold resistance to leather. No adverse reports regarding it have been published. I. D. C.

"Servarin" Dehairing Agent and "Plantachrom." Two New Special Products for the Leather Industry. By J. Mahler. *Oesterreichische Leder-Zeitung*, **6,** 314 (1951). Two products of Josef Mahler & Co., Villach-Seebach (Austria) are described. Servarin is an unhairing agent the action of which is based on different amines and a simultaneous enzyme action. Plantachrom is a combination tanning material containing chrome and a synthetic base. I. D. C.

The Vegetable Tannins with Special Reference to Chestnut Tannin. By E. Durio and G. A. Bravo. *Osterreichische Leder-Zeitung*, **6,** 339, 367 (1951). A lecture, reviewing vegetable tanning materials in general and neutralized chestnut extract in particular. I. D. C.

Practical Use of Hausruck Extract. By K. Blach. *Osterreichische Leder-Zeitung*, **6,** 372 (1951). Practical advice is given on the use of Hausruck extract—a beech lignin extract. I. D. C.

The Examination and Evaluation of Fish Oils. By V. Czepelak. *Oesterreichische Leder-Zeitung*, **6,** 392 (1951). A lecture discussing practical and chemical tests for evaluating fish oils. Color, odor, turbidity give clues as to quality. For chamois leather tanning, unsaponifiable matter is of no value, mineral oil interferes with the washing to remove excess oil, and oxidized fatty acids darken the leather and do not wash out. The acid number should be approximately 30 for best results and must not be less than 14; if the iodine number is over 160, oxidation may be too rapid and the temperature may reach too high a value. I. D. C.

Modern Work Processes in the Leather Industry. By R. Bosse. *Oesterreichische Leder-Zeitung*, **6,** 396 (1951). A lecture devoted principally to a discussion of the Tanigans. Although syntans are more expensive than imported, natural tannins, their extra cost is offset by the saving in vegetable tannin because syntans retard mold growth and loss of the

latter. Increased fullness in leather to be dried by the pasting process can be obtained by retanning with syntan or by replacing part of the bicarbonate, in the neutralization, with syntan. There are 60-80 syntans on the market so the tanner has difficulty in finding the best for his purpose. I. D. C.

Observations on the Pasting Process. By K. Eitel. *Osterreichische Leder-Zeitung*, **7**, 37 (1952). A lecture describing pasting equipment and advantages of the process. I. D. C.

Progress Report for the Period August 1, 1950 to July 31, 1951. (Research Institute for the Leather Industry, Vienna). By J. A. Sagoschen. *Oesterreichische Leder-Zeitung*, **7**, 14, 41, 66 (1952). Report of the Institute and the School for Foremen. Summaries are given of analyses of samples submitted to the Institute. The samples included practically all the materials used in tanneries, from raw stock and crude tanning materials to finished leather. I. D. C.

Concerning Fir (Pine) or Beech Waste Liquors as Raw Materials for Lignin Tanning Extracts. By A. W. Sohn and E. Roser. *Das Leder*, **2**, 207 (1951). Sagoschen (*This Jour.* **46**, 426) has indicated beech wood is preferable to fir (Fichte) for making lignin tanning extract. The authors were unable to find a decided difference in behavior of these woods during digestion. The extracts were similar, except that Hausruck extract (from beechwood) was somewhat darker and lower in purity. Tanning with lignin extract alone is a matter of tanning procedure, especially acidity, and not of source of the lignin. I. D. C.

The Sensitivity to Lime of Anionic Leather Dyes. By G. Otto. *Das Leder*, **2**, 210 (1951). Tanners normally use ordinary tannery water in the dye vats; but lime, in hard water, may influence dyeing. To test the effect of lime on various dyes a dispersion of calcium carbonate containing 74 grams of CaO per liter was prepared by passing carbon dioxide into a lime suspension until the pH value was 7.6, then passing the suspension through a homogenizer. To 10 cc. of dye solution containing 1/1500 mol of pure dyestuff, 1 cc. of the calcium carbonate suspension was added and left overnight. Dye in solution was then determined with a colorimeter. Eight acid and 14 substantive dyes were tested. Acid dyes were absorbed only slightly or not at all. The following substantive dyes were completely precipitated: Congo brown G, Plutoform black BL, Benzochrom brown G, Benzochrom brown R, Congo brown R, Diamin brown B and Diamin brown M. From a study of the structural formulas of the dyes the following conclusions were reached: Dyes react with lime if (1) the dye has a positive nucleus with 2 amino groups and no sulfo group is present to make the nucleus negative, (2) an aromatic nucleus carries 2 hydroxyl groups or (3) a naphthol nucleus carries an amino group. A carboxyl group is quite effective, especially if present as a salicyclic acid or phenylglycine radical. I. D. C.

The Sensitivity to Lime of Anionic Dyes. By K. Eitel. *Das Leder*, **3**, 56 (1952). (see preceding abstract). Criteria based on molecular weight and constitution of a dye are of little practical value, because they are seldom known by the tanner. Sensitivity to lime (temporary hardness) as described by Otto can be counteracted in the dye bath by use of acetic acid. Permanent hardness is a more serious problem. A solution having a hardness of 10 degrees (100 mg. CaO/liter) can be made by dissolving 259 milligrams of crystalline calcium chloride ($CaCl_2 \cdot 6H_2O$) and 147 milligrams of Epsom salt ($MgSO_4 \cdot 7H_2O$) in a liter

of water. A practical test for stability of a dye to hard water is as follows: Dissolve 0.2 grams of dye in 100 cc. of distilled water. Dilute 10 cc. portions of the dye to 200 cc. with distilled water and with solutions having permanent hardness values of 10, 20, 30 and 40 degrees. After 1 hour or 24 hours examine the solution in a bright light for a precipitate. A change in strength or shade of dye should be noted. A reliable standard dye is required. Although dyeing action is usually better if stability to hard water is good, no general conclusions regarding dyeing behavior in hard water are possible from the hard-water stability test. I. D. C.

The Purification of Tannery Waste Liquors. By W. Merkel. *Das Leder*, **3**, 9 (1952). A description is given of equipment for filtering, screening, clarifying, or settling tannery affluents. In Germany, metallic iron or iron sulfate, whichever is cheaper, is used for clarification, although at times when tannin is present the more expensive aluminum sulfate must be used. For biological purification, tannery waste requires a threefold dilution with household sewage. Treatment of wastes is required by law, but degree of purification is not regulated as yet. Maintaining the pH between 6 and 8 and limiting settleable matter to 5 milligrams of dry matter or 0.25 cc. wet sludge per liter is adequate and attainable. I. D. C.

The Difference Between Tannin and Nontannin Components of Oak Bark. By A. Küntzel and A. Zissel. *Das Leder*, **3**, 2 (1952). A semi-commercial extract of oak bark containing 20 per cent tannin was separated into three fractions by the following procedures: Fraction I was precipitated by adding alcohol until the alcohol-water ratio was 80-20. The filtrate was evaporated in a vacuum with addition of water until all alcohol was removed. The dry product was then extracted with absolute alcohol to yield Fraction III. Fraction II was that portion that was insoluble in absolute alcohol. Analyses of the fractions are shown in the following table, the results being expressed as percentage of total dry matter:

	Unfractionated	Fraction I	Fraction II	Fraction III
Tannin	57.6	58.3	54.2	49.1
Nontannin	40.7	37.3	42.7	49.8
Insolubles	1.7	4.4	3.1	1.1
Tan value	83.5	57.5	81.9	99.5
Combining value	52.4	28.9	48.3	57.3

Fraction I did not penetrate skin completely and the tanned skin was dark and hard. Fractions II and III produced soft, light colored leather. Qualitative tests indicated I was of the pyrogallol class and III of the catechol class. Paper chromatograms for I and III (II?) were not very different in daylight, which shows the tannins, but were quite different in ultra violet light which makes visible the nontannins. Ultra violet absorption curves for II and III had maxima at 260 to 280 millimicrons, as is true also for quebracho and mimosa. In fraction I the tannin component was lacking. Haglund *(This Jour.*, **46,** 689) found that fraction I of spruce (pine) bark consisted largely of salts of weak organic acids and the same was true of oak bark. By ion exchange and titration, fraction I was found to contain 215 milliequivalents of cation and III, 27.5 milliequivalents. By dialysis of I, 52 per cent of the cation was removed, showing that half of the cation is in the form of a low molecular salt and the other half is combined with a high molecular tannin or nontannin. In 80 per cent alcohol, fraction I dissolved if a few drops of acid were added and increased if alkali was added. Extracts like quebracho that are completely soluble in dilute alcohol, yield a fraction I if a small amount of alkali is added. The question then arose, as to whether the

poor tanning ability of fraction I was due (1) to its salt character, (2) the presence of certain nontannins, or (3) a constitutional difference between the tannin of fraction I and those of fractions II and III. To answer this question, the pure tannin was separated from fraction I. A satisfactory separation of tannin and nontannin could not be made with hide powder, so the tannin was precipitated as the lead salt. Recovery of the tannin from the lead tannate was difficult because of the presence of a trace of gel-forming nontannin in the precipitate. The tannin dissolved in warm water and was not precipitated by alcohol. This confirms the belief that the alcohol precipitate consists of salts. The tannin gave a brown precipitate with gelatin, no precipitate with either bromine or formaldehyde-hydrochloric acid and had a purity of 89 by analysis. Tanned hide powder was dark brown and hard, but the purified tannin, even when brought to pH 6.2 with alkali, was a better tanning agent than fraction I. The nontannin therefore was partly responsible for the poor tanning ability, but the nature of the tannin was the principal factor. The tannin had a high acidity and required 205 cc. of normal sodium hydroxide per 100 grams for neutralization, whereas only 101 cc. were required by the tannin of fraction III. This strong acid combines with cations from the nontannins and so becomes precipitatable by alcohol. After oxidation with hydrogen peroxide, one third of fraction II became insoluble in 90 per cent alcohol. Fraction III, after oxidation, did not precipitate with alcohol because no cations were present. The nontannin of fraction I was a light brown powder that formed a viscous gel-like mass when moistened with water. Fraction III was easily separated into tannin and nontannin by precipitating the tannin as the lead salt. The pure tanin was soluble in dilute solution, but a concentrated solution was cloudy. The tannin was less astringent than the whole fraction. Solubility and astringency were improved by a nontannin constituent that could be extracted with ether from either the tannin or the entire fraction III. This substance, called nontannin IIIb, was 3 per cent of the original extract. It gave a cloudy solution with bromine, gelatine, or formaldehyde-hydrochloric acid and a blue color with iron salts. Leather tanned with IIIb present was softer and more leather-like than leather tanned with IIIb absent. A nontannin fraction IIIa was prepared by extracting IIIb from fraction III with ether, then removing tannin with hide powder. This fraction was entirely different from IIIb. It was evident that nontannin IIIb contained a hydrotropic substance that (1) stabilized the tannin of fraction III in aqueous solution and (2) had a hydrotropic swelling effect on collagen. During tanning, IIIb is taken up first by the hide powder, causes swelling, then is replaced by tannin. The tannin appears to drive IIIb before it. From its action on hide substance it follows that nontannin IIIb is chemically related to tannin III and differs from the latter principally in degree of polymerization. Ultraviolet absorption curves for fraction III and the purified tannin of this fraction were nearly the same because of the similarity of the tannin and nontannin; for fraction I the curves for the whole fraction and for the purified tannin were quite different. In summary, oak bark was found to contain two types of tannin. One was a high-grade phenolic tannin ranging in particle size from the phenolic nontannins through the true tannins, to the insoluble phlobaphenes. The second group of tannins had a much higher acidity than the first group and probably is formed from the latter by oxidation. The system contains tannins ranging in acidity from low to high. The nontannins are as important as the tannins with respect to their effect on tanning

I. D. C.

Discoloration of Leather by Chlorophyll. By O. Engel. *Das Leder*, **3**, 14 (1952). Leather may be stained by chlorophyll, if it is tanned with ground sumac leaves. Concentrated extracts contain little chlorophyll because it separates when the extract is evaporated. Sumac stains can be removed with acetone but this also removes some tannin. Ultraviolet light bleaches the surface chlorophyll. Stains may appear only after currying and if

bleached, may reappear later. Detection of chlorophyll in finished leather is difficult; chemical methods can not be used, only the spectroscopic method. Staining is least with Italian sumac; more frequent with Bulgarian and Spanish sumac and also with cultivated staghorn sumac. I. D. C.

Characterization of Deliming Agents Through Potentiometric Titration? By J. Plapper. *Das Leder*, **3**, 25 (1952). Deliming agents are usually evaluated by titration with alkali to phenolphthalein. A better method is to make a potentiometric titration covering the range pH 2 to 11. From the titration curve one can determine the following: (1) the number of equivalents of acid per 100 cc. or 100 grams of the deliming agent, (2) the strength of the acids and bases in the agent (their dissociation constants), and (3) the buffer range and bufffer strength. I. D. C.

Investigations on the Formation of Simple, Masked Chrome Complexes. I. A Conductometric Method for Determining the Stoichiometric Composition of Masked Chrome Complexes with Homogeneous Attached Groups. By A. Küntzel, H. Erdman and H. Sparkäs. *Das Leder*, **3**, 30 (1952). Masking of chromium chloride was studied by means of conductometric measurements in solutions containing 0.1 per cent chromium (Cr) and 1, 2, 4, 6 and 8 equivalents (based on Cr) of sodium formate, sodium acetate, or sodium oxalate resp. Immediately after addition of sodium formate, conductivity decreased rapidly, then after a few hours remained apparently constant, although there was a slow decrease lasting for several weeks. The initial decrease in conductivity was the same with 6 as with 4 equivalents of formate. The same types of conductivity-versus-time curves were obtained with sodium acetate as with formate, except that complex formation ended with 3 equivalents of acetate instead of 4 as with formate. On addition of up to 4 equivalents of sodium oxalate the bright green color of the chromium chloride solution changed to red-violet, then to violet-tinged green after 6-8 equivalents were added. After the initial drop there was no further decrease in conductivity with oxalate. Alkali titration curves (conductivity versus ml. of N/200 sodium hydroxide) were obtained on masked, aged chromium chloride solutions after dilution 200-fold. The conductivity of partly masked solutions decreased with the first addition of alkali, as a result of neutralization of the free acid from hydrolysis. After the initial drop the curve was flat during precipitation of the chromium hydroxide. Finally it rose rather rapidly when alkali was present in excess. Fully masked solutions showed little or no initial drop (no free acid was present) and the flat portion of the curve was absent because the masked salt did not precipitate. Acid titration curves were also obtained on aged, masked solutions. The complex was so stable that it was not affected by the titration. The unreacted masking salt was determined by comparing the titration curve with curves obtained by titrating solutions of pure masking salt in concentrations corresponding to from 0 to 5 equivalents, based on the chromium concentration in the chromium chloride solution (N/3460). The results show that 1.7 equivalents of sodium formate had entered into the formate complex. Heating in a sealed tube for 10 minutes at 100° increased the formate in the complex to 2 equivalents. The acetate complex contained exactly 2 equivalents. On heating in a sealed tube, a new, distinct complex containing 3 equivalents of acetate was formed. Four equivalents (2 mols) of oxalate reacted completely with the chromium to form the complex. A definite crystalline complex salt of this type is well known and has been thoroughly investigated. (Stiasny, Chromgerbung). If either 6 or 8 equivalents of oxalate were present the complex contained 5 equivalents. I. D. C.

Determination of Power Requirements of Drums. By H. Diekmann. *Das Leder*, **3**, 37 (1952). Power required to drive a drum is usually calculated by multiplying the weight of solids in the load by revolutions per minute. The following formula for a dry load is more nearly exact:

$$L = K_1 G r w \left(1 + \frac{3}{2} \frac{r w^2}{g}\right)$$

where L is power in kilogram meters per second, G is load in kilograms, r is radius of the drum in meters, w is angular velocity per second, g is the gravity constant in meters per second and K_1 is a constant. The value of K_1 varied from 0.39 to 0.47 and was found by trials with drums of different sizes run at various speeds with increasing loads. When float was added to the system, a second constant K_2 was required. K_2 varied from 0.34 to 2.04, depending on conditions. I. D. C.

Investigation on the Formation of Simple, Masked Chrome Complexes. II. The Complex Activity of the Sulfate Ion. By A. Küntzel, H. Erdmann and H. Sparkäs. *Das Leder*, **3**, 49 (1952). Chromium sulfate solutions are more complicated than chromium chloride solutions, because in the former sulfate has already entered the complex and the salt is masked. This is especially true for ready-made tanning liquors, self-reduced liquors and chrome alum solutions prepared hot. Sodium sulfate is a masking salt. Its masking action was studied in aged chromium chloride solutions. Chromium sulfate could not be used because it is already masked. On addition of 1, 2 or 4 equivalents of sodium sulfate to a 0.1 per cent chromium chloride solution there was at first a slight drop in conductivity, then a very slow uniform drop accompanied by a change in color from violet to green. The conductivity of the sodium sulfate and chromium chloride solution was less than that of a potassium chloride and chromium chloride solution, due to buffering. Sodium chloride had no masking action. In conductivity-titration curves for sodium sulfate and sodium chloride the middle portion (region of precipitation of chromium hydroxide) sloped upward showing masking, but there was a sharp end point, indicating that the sulfate complex is decomposed by alkali. The maximum uptake of sulfate was 8 equivalents at room temperature. Upon boiling, more sulfate entered the complex but the amount could not be measured by the conductivity method. I. D. C.

Leather Damage caused by the Vertical Blood Vessels in the Hide. By A. Küntzel. *Das Leder*, **3**, 53 (1952). Two types of damage, apparently from the same cause, were observed. One type consisted of raised spots the size of rice grains on the grain surface of the leather. The other damage was found in chrome leather when shaving to a wedge to form a splice for belting. The damaged areas were softer than the undamaged and did not adhere after gluing. The damage was in areas surrounding the vertical blood vessels in the reticular layer. It probably was caused by enzyme diffusing through the blood vessel walls during delayed salting in warm weather. I. D. C.

PATENTS

Tanning. Brit. Pat. 628,989. J. R. Evans & Co., Oct. 3, 1946. Hides, skins and pelts are tanned in an acid-reacting aqueous medium containing resorcinol or pyrogallol and an aldehyde selected from formaldehyde, polymers of formaldehyde, acetaldehyde, crotonaldehyde, benzaldehyde and furfural at a *p*H of 0.3—3.0. Strong acids such as sulphuric, hydrochloric, phosphoric or oxalic are used to produce the required *p*H in the tanning liquor which is subsequently neutralized by the addition thereto of alkaline materials such as borax, sodium carbonate, sodium bicarbonate, sodium acetate, sodium formate, sodium thio-

sulphate, ammonium bicarbonate, or hexamethylene tetramine. The process may be combined with other tanning operations, e.g., resorcinol-formaldehyde tannage immediately followed by chrome or zirconium tannage.

The Specification as open to inspection under Sect. 91 refers to the use of nuclear substituted derivatives of resorcinol and pyrogallol which may wholly or in part replace the resorcinol or pyrogallol. Thus, resorcinol may be replaced wholly or in part by hexyl, tertiary octyl, benzyl, phenyl- or methoxy-resorcinol. This subject-matter does not appear in the Specification as accepted.

Leather Making. Brit. Pat. 627,637. E. G. Wilson. March 25, 1947. Apparatus for pit tanning or liming of hides or skins by repetitive rolling and unrolling in the liquor.

Preservation of Hides and Pelts. Brit. Pat. 656,232. C. H. Gibson. March 1, 1947. Hides and pelts are preserved for storage or transit in a continuous process occupying 2.5 hours (as compared with 20 days required for liming or beam house operation), with many advantages, by dehairing, bating, washing, bisulfiting, washing again, neutralizing, then drumming in presence of salt (1.7), $NaHSO_3$(1.33), sulfonated neatsfoot or fish oil (0.001), and 40 per cent aqueous formaldehyde (0.0005) while adding a solution of H_2SO_4 (1 per cent on salt weight) in water. A procedure for conditioning the conserved hides just prior to tanning, is also described.

Tanning Hides or Skins. Brit. Pat. 655,094. J. S. F. Abaye, April 30, 1948. Hides or skins are tanned by using approximately 33 per cent of the normal tanning agent, neutralizing, and the freezing of the material to –30°. The temperature is raised to –2° until the material is completely dry, when the tanning process is complete.

Tanning Leather. Brit. Pat. 628,741. J. R. Evans & Co., April 24, 1946. Animal skins which may be previously pickled, are tanned by an aqueous solution containing 1—12 per cent free melamine on the basis of the wet weight of the skins, and more than one, but less than three, mols. free formaldehyde per mol. of melamine, the melamine and formaldehyde remaining substantially unreacted at the beginning of the process, the resulting solution having a *p*H of 4—5.5, and the action being continued for 3—21 hours. Chrome-tanned leather may also be retanned without previous detanning. Several examples are given, referring inter alia to the presence of salt, sodium acetate, acetic acid, and (in one example), basic zirconium acetate in the tanning liquor, and to subsequent fat-liquoring of the tanned skins with a mixture of raw neatsfoot oil and sulphonated oil, and pigmenting with clay and titanium dioxide.

Tanning and Currying Leather. Brit. Pat. 628,818. American Cyanamid Co., July 23, 1946. Hides or leather are treated, preferably in a tanning drum, with a condensation product of a methylol derivative of melamine and/or urea and an amino carboxylic or amino sulfonic acid or salt thereof. Preferably aqueous solutions are used—dilute for tanning and more concentrated for bleaching. The treated leather may be washed and fatliquored and pigmented. For use for filling leather the compositions may be heated at pH 5-7 to increase their viscosity. In an example, chrome retanned side leather was washed and drained and treated with an aqueous alkaline solution of a sulphanilic acid-methylol melamine condensation product. Drumming was continued for 45 minutes and the leather fat-liquored, pigmented and horsed up. In a second example, dyed leather was treated with an aqueous solution of the condensation product containing also logwood and copperas. After the treatment a top dye was applied. Solution containing dye can also be applied to uncolored leather.

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Na Cl	0.40
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Na_2S	61.00

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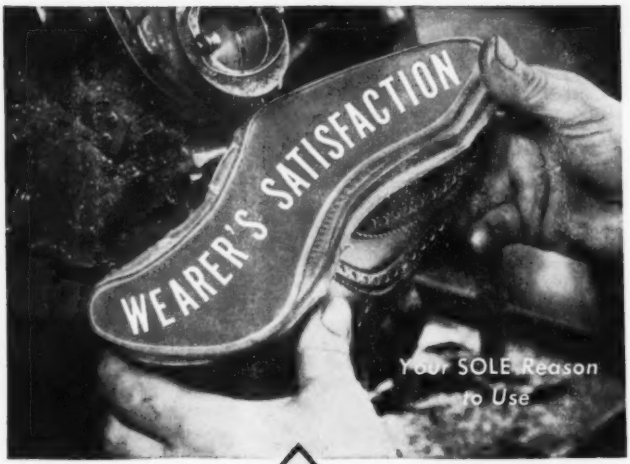

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